TECHNICAL METHODS OF CHEMICAL ANALYSIS

LUNGE AND KEANE'S

TECHNICAL METHODS

OF

CHEMICAL ANALYSIS

SECOND EDITION

EDITED BY

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PREFACE

THE previous edition of *Technical Methods of Chemical Analysis* was based on the work *Chemisch-technische Untersuchungsmethoden*, originally edited by Dr F. Böckmann and subsequently revised in several editions by Professor Lunge.

The English translation was edited in conjunction with Professor Lunge, and was adapted to English conditions of manufacture by collaboration with specialists fully familiar with the methods of work in use in this country. Although this adaptation was made as complete as possible, it was necessarily somewhat hampered by the character and subject-matter of the German text, and it has accordingly been considered preferable to make this new edition more independent, and each of the contributors entirely responsible for his section.

From this consideration many of the sections have been largely rewritten, several new sections have been added, and the whole of the subject-matter has been thoroughly revised and brought up to date. The arrangement of the contents of each volume has also been modified so as to group the sections dealing with correlated industries more advantageously than in the previous edition.

This plan was fully approved by Professor Lunge, although at the time the preparation of this new edition was begun, he was unable to participate in any way in the editorship. It is a matter of sincere regret that he has not lived to see the completion of the work to which he made such important contributions by his outstanding services to the advancement of industrial analysis.

The work will be published in six separate volumes, and in addition to the index with each volume, a complete index for the whole will be provided. The tables of general applicability are printed for reference at the end of each volume, and an index of tables has been added.

The new sections included in the present volume are—"Electrolytic Methods of Chemical Analysis" and "Physical Methods employed in Chemical Analysis."

As in the previous edition, all the numerical data, with the exception of those in which empirical factors are employed in technical work,

are calculated from the table of atomic weights for 1921-23, with O=16 as basis, issued by the International Committee on Atomic Weights. The numerical data for gases and for the weights of substances to be taken for analysis, so as to correspond to definite volumes of gases, are all calculated from the *real* litre weights according to the most reliable determinations, not from the calculated values. All temperatures are given in Centigrade degrees except where otherwise stated.

The Editors desire to record their thanks to the Faraday Society, the Society of Chemical Industry, and Messrs John Wiley & Sons, for permission to reproduce illustrations from their publications, and to Messrs Baird & Tatlock (London), The Cambridge and Paul Scientific Instrument Co., Messrs Evershed and Vignolles, the Editor and Publisher of the *Gas World*, Messrs A. Gallenkamp & Co., Messrs Charles Griffin & Co., Messrs J. & J. Griffin & Co., Messrs Adam Hilger & Co., Messrs Longmans, Green & Co., Messrs Siebe, Gorman & Co., Messrs W. Sugg & Co., Messrs Thompson, Skinner & Hamilton, and Messrs Alex. Wright & Co., for the loan of illustration blocks.

CHARLES A. KEANE.
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Saltcake and Hydrochloric Acid.

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Sodium Carbonate.

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Cyanogen Compounds.

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ABBREVIATED TITLES OF JOURNALS

ABBREVIATIONS.	JOURNALS.
Acetylene	Acetylene
Amer. Chem. J.	American Chemical Journal
Amer. J. Sci.	American Journal of Science
Analyst	The Analyst
Annalen	Annalen der Chemie
Ann. Physik	Annalen der Physik
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Annali Chim. Appl.	Annali di Chimica Applicata
Ann. Chim. Phys.	Annales de Chimie et de Physik
Ann. Falsif.	Annales des Falsifications
Apoth.-Zeit.	Apotheker-Zeitung
Arch. Pharm.	Archiv der Pharmacie
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei
Berg u. Hütten. Zeit.	Berg und Hüttenmännische Zeitung
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deutsch. Physik. Ges.	Berichte der deutschen physikalischen Gesellschaft
Biedermann's Zentr.	Biedermann's Zentralblatt für Agricultur Chemie
Boll. chim. farm.	Bollettino chimico farmaceutico
B. P.	British Patent
Brewer's J.	Brewer's Journal
Brit. and Col. Drug.	British and Colonial Druggist
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine
Bull. Assoc. Belg. des Chim.	Bulletin de l'Association Belgique des Chimistes
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association chimique de Sucre et de Distillerie
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris
Bull. Soc. Ind. Nord	Bulletin de la Société Industrielle du Nord de la France
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse
Chem. News	Chemical News
Chem. Trade J.	Chemical Trade Journal
Chem. Zeit.	Chemiker Zeitung
Chem. Zeit. Rep.	Chemiker Zeitung Repertorium
Chem. Ind.	Chemische Industrie
Chem. Rev. Fett-Ind.	Chemische Revue über die Fett- und Harz-Industrie
Chem. Zentr.	Chemisches Zentralblatt
Chem. and Drug.	Chemist and Druggist
Chem. Weekblad	Chemisch Weekblad
Comptes rend.	Comptes rendus hebdomadaires des séances de l'Académie des sciences
Dingl. polyt. J.	Dingler's polytechnisches Journal
Electrician	Electrician

ABBREVIATIONS.	JOURNALS.
Electrochem. Ind.	Electrochemical and Metallurgical Industry
Electrotech. Zeitsch.	Electrotechnische Zeitschrift
Engineer	Engineer
Engineering	Engineering
Eng. and Min. J.	Engineering and Mining Journal
Farben-Zeit.	Farben-Zeitung
Färber-Zeit.	Färber-Zeitung
Fischer's Jahresber.	Fischer's Jahresbericht
Gas J.	Gas Journal
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Gerber	Der Gerber
Gerber Zeit.	Deutsche Gerber Zeitung
Ger. Pat.	German Patent
Gummi-Zeit.	Gummi-Zeitung
Helv. Chim. Acta	Helvetica Chimica Acta
India-rubber J.	India-rubber Journal
Ind. Bl.	Industrie Blatt
Int. Sugar J.	International Sugar Journal
Jahresber. d. chem. Techn.	Jahresbericht der chemischen Technologie
Jahresber. d. Pharm.	Jahresbericht der Pharmazie
Jahresber. f. Chem.	Jahresbericht fur Chemie
J. Agric. Sci.	Journal of Agricultural Science
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Anal. and Applied Chem.	Journal of Analytical and Applied Chemistry
J. Chem. Met. Soc., S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa
J. Chem. Soc.	Journal of the Chemical Society
J. Chem. Soc. Abstr.	Journal of the Chemical Society, Abstracts
J. Franklin Inst.	Journal of the Franklin Institute
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers
J. Inst. Metals	Journal of the Institute of Metals
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Phys. Chem.	Journal of Physical Chemistry
J. prakt. Chem.	Journal für praktische Chemie
J. Physik	Journal der Physik
J. Physique	Journal de Physique et le Radium
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists
Kolloid Z.	Kolloid Zeitschrift
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Leather Tr. Rev.	Leather Trades Review
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West
Mitt. techn. Gew. Museums	Mittheilungen des technischen Gewerbemuseums in Wien
Mitt. Zentralst. Wiss.-tech. Unters.	Mittheilungen aus der Zentralstelle für wissenschaftlich-technische Untersuchungen
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien

Abbreviations.	Journals.
Monatsschrift f. Text.-Ind.	Monatsschrift für Textil-Industrie
Monit. Scient.	Moniteur Scientifique
Nuovo Cimento	Il Nuovo Cimento
Oesterr. Chem. Zeit.	Oesterreichische Chemiker Zeitung
Oesterr.-Ungar Zeitschr.	Oesterreichisch-Ungar Zeitschrift für Zuckerindustrie und Landwirthschaft
Paper and Pulp	Paper and Pulp
Papier-Zeit.	Papier-Zeitung
Petrol. Rev.	Petroleum Review
Pharm. J.	Pharmaceutical Journal
Pharm. Rev.	Pharmaceutical Review
Pharm. Weekblad	Pharmazeutisch Weekblad
Pharm. Zeit.	Pharmazeutische Zeitung
Pharm. Zentralh.	Pharmazeutische Zentralhalle
Pharm. Zentr.	Pharmazeutisches Zentralblatt
Phil. Mag.	Philosophical Magazine and Journal of Science
Phil. Trans.	Philosophical Transactions of the Royal Society
Phys. Rev.	Physical Review
Proc. Amer. Acad.	Proceedings of the American Academy
Proc. Amer. Electrochem. Soc.	Proceedings of the American Electrochemical Society
Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng.	Proceedings and Bulletin of the American Institute of Mining Engineers
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. Inst. Min. and Met.	Proceedings of the Institution of Mining and Metallurgy
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Edition)
Proc. Phys. Soc.	Proceedings of the Physical Society of London
Rev. Gen. Mat. Col.	Revue Générale des Matières Colorantes
Rev. intern. Falsif.	Revue internationale des Falsifications
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique
Roy. Soc. Proc.	Proceedings of the Royal Society
Scient. Amer.	Scientific American
Stahl u. Eisen	Stahl und Eisen
Staz. speriment. agr. Ital.	Le Stazione sperimentali agrarie Italiane
Tonindustrie Zeit.	Tonindustrie Zeitung
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy
U.S. Cons. Reps.	United States Consular Reports
West Ind. Bull.	West Indian Bulletin
Woch. f. Brau.	Wochenschrift für Brauerei
Z. anal. Chem.	Zeitschrift der analytischen Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie
Z. anorg. Chem.	Zeitschrift der anorganische Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie
Z. Farb. Ind.	Zeitschrift für Farben Industrie
Z. Farb.- u. Text.-Chem.	Zeitschrift für Farben- und Textil-Chemie
Zeitschr. f. landw. Versuchswesen, Österr.	Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich
Z. für chem. Apparatenkunde	Zeitschrift für chemische Apparatenkunde

Abbreviations.	Journals.
Z. ges. Brauw.	Zeitschrift für das gesammte Brauwesen
Z. ges. Schiess- u. Sprengstoffw. .	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen
Z. Instrumentenk. . . .	Zeitschrift für Instrumentenkunde
Z. öffentl. Chem. . . .	Zeitschrift für öffentliche Chemie
Z. physik. Chem. . . .	Zeitschrift für physikalische Chemie
Z. Spiritusind.	Zeitschrift für Spiritusindustrie
Z. Unters. Nahr. u. Genussm. .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel
Z. Ver. deut. Zuckerind. . .	Zeitschrift des Vereins der deutschen Zucker-Industrie
Z. Verein. deutsch. Ingen. . .	Zeitschrift des Vereins deutscher Ingenieure
Z. Zuckerind. Böhm. . . .	Zeitschrift für Zuckerindustrie in Böhmen

CONTENTS OF VOLUME I.

TECHNICAL METHODS OF CHEMICAL ANALYSIS

INTRODUCTION

TECHNICAL methods of chemical analysis include many general analytical methods together with certain practical tests which have been devised to meet the requirements of the manufacturing processes of chemical industry. The latter comprise a number of methods which now form a recognised part of analytical chemistry, but which were originally looked upon as purely "technical" methods. This is particularly true of volumetric analysis, which, founded as early as 1795 and 1806 by Descroizilles, was first used as a method for controlling and estimating the value of technical products such as acids and alkalis. Gay-Lussac's methods for chlorimetry (1824), alkalimetry (1828), and for the estimation of silver (1832), as well as the permanganate method of estimating iron introduced by Margueritte (1846), fall in the same category, and were all devised to meet the requirements of technical work, and were at first employed exclusively for this purpose.

"Volumetric" analysis was, for a considerable period, regarded with a certain degree of contempt as a "technical" method, the study of which could only be disadvantageous to the attainment of scientific accuracy. This view could, however, no longer be upheld after it was shown by Bunsen, in his paper on volumetric analysis by means of iodine (1853), that the accuracy of this process was greater than that of most gravimetric methods, and after other investigators, especially H. Schwarz (1850) and Friedrich Mohr (from 1855), had established the value and reliability of this branch of analysis.

On the other hand, many technical methods have been developed from the more accurate and lengthy processes employed in scientific investigation, as in the case of the technical methods of gas analysis which are based on the classical investigations of Bunsen (1857).

These reciprocal developments have placed a wide field of analytical processes at the disposal of those engaged in technical work. Their applicability is related to the analytical control required; they have

been modified and adapted so as to meet these requirements, especially in relation to rapidity, degree of accuracy and simplicity in manipulation, in accordance with the character of the operations and materials concerned.

The technical methods of chemical analysis comprise the following classes of work :—

1. Examination of Raw Materials

Accurate methods of analysis are generally employed. In other cases, rougher tests may be sufficient within limits, and in part must suffice in default of better methods; physical, microscopic, or other external methods of examination are also often used.

2. Control of Working Conditions

Chemical analysis, with the addition, in many cases, of physical methods (*e.g.*, specific gravity determinations, pressure relations, temperature control, etc.), is adopted. The methods usually employed are those which can be carried out with the greatest possible rapidity; they are consequently often lacking in accuracy, but suffice for comparative purposes.

3. Examination of Final Products

Accurate methods of analysis are sometimes employed, especially when a guarantee of composition is required; frequently, however, easily observable external characteristics and empirical tests suffice.

In all three classes different methods of examination may be necessary, namely :—

(*a*) **Qualitative tests,** which are in most cases concerned with the detection of an impurity.

(*b*) **Quantitative determination of a principal constituent,** which is the subject of a guarantee in buying or selling, or which is a leading factor in the working of a process.

(*c*) **Quantitative determination of secondary constituents,** in which various considerations demand attention, namely :—

- (α) Secondary constituents of value which form the subject of a guarantee, such as the percentage of carbon in steel.
- (β) Secondary constituents which are deleterious impurities, and which ought not to exceed a certain maximum, *e.g.*, phosphorus in steel, chlorides in potassium nitrate.
- (γ) Secondary constituents the estimation of which serves for the indirect determination of the amount of the principal constituent present, as in the valuation of Chili saltpetre.

(*d*) **Quantitative determination of several constituents,** usually a combination of the two classes *b* and *c*, *i.e.*, the estimation of the chief constituent and of one or more important impurities, as the estimation of the alumina, iron, and free acid in the analysis of aluminium sulphate, and the determination of the iron, sulphur, and phosphorus in the examination of iron ores.

(*e*) **Examination of certain physical properties,** *e.g.*, the viscosity of lubricating oils, the flash-point of petroleum, the specific rotatory power of sugars.

(*f*) **Examination of certain external properties demanded by the trade,** such as colour, lustre, density, strength, etc.

(*g*) **Complete chemical analysis** is only very exceptionally required for technical purposes; it may be necessary in such instances as a new discovery of ores and the like.

These classes of analytical work will all be considered in the sections dealing with the various industries. A general knowledge of analytical chemistry, and more especially of mineral analysis and of elementary organic analysis, is premised. The special apparatus and methods of work described are those requisite or useful for the attainment of the results that are required in technical work, even in those instances in which general methods of analysis are employed. The greater part of the book, however, is naturally devoted to the methods which have been specially worked out for technical purposes, and which are but seldom if ever practised in scientific laboratories.

The methods and apparatus described in the first part of this volume are those used for a variety of purposes, particular stress being laid upon those considerations that serve to facilitate the work of technical laboratories. From this standpoint descriptions are included of the apparatus and methods employed in electro-chemical analysis and of the physical methods of examination employed in technical work. The more specific methods of analysis employed in the various industries are dealt with in the subsequent portion of this volume and in the succeeding volumes.

GENERAL METHODS USED IN TECHNICAL ANALYSIS

By CHARLES A. KEANE, D.Sc., Ph.D., and the late Professor G. LUNGE

I.—THE TAKING OF SAMPLES[1]

THE preparation of an average sample, really representative of the quality of the material to be investigated, requires special care and precautions. It is a problem of fundamental importance in all branches of technical analysis, as lack of care and judgment in sampling necessarily invalidates subsequent analytical results.

The preparation of a really average sample is most difficult in materials occurring in large pieces; it is considerably easier with more finely grained materials, still easier with powdered materials, easiest of all, as a rule, with liquids, and more difficult with gases. Special difficulties occur when contact with air, whilst the sample is being taken and ground, may alter its condition by evaporation, absorption of water, oxidation, etc. In such cases very special precautions are necessary, which will be fully dealt with subsequently.

With materials in lumps, sampling is most difficult when the valuable constituent occurs only in small amount and very unequally distributed, as in ores of the noble metals, or when certain very deleterious impurities, also unequally distributed, are present. The disputes that have arisen from defective sampling have led to the drawing up of definite rules for sampling; also, it has become the custom, in all important cases, for the operations of taking samples, grinding them, and making them into a form ready for handing to the chemist, to be carried out in the presence of representatives of both parties concerned, or in the presence of a mutually appointed referee. Usually several bottles are simultaneously filled with the prepared average sample, and closed with the seal of both parties.

[1] *Literature on Sampling.*—W. Glen, *J. Soc. Chem. Ind.*, 1898, **17**, 123; M. L. Griffin, *ibid.*, 1905, **24**, 183; 1909, **28**, 192; W. L. Baillie, *Chem. Trade J.*, 1920, **67**, 333.

The following directions lay no claim to be a permanent solution of the difficult problem of sampling; they can only represent an approximation which has been found to be generally satisfactory.

In many cases, particularly in the industries connected with organic chemistry, but also, *e.g.*, with caustic soda, fuming sulphuric acid, metals, alloys, etc., the samples must be taken according to special methods applicable to each individual case, owing to the nature of the substances in question. Where standardised or statutory methods of analysis have been adopted, as in the case of artificial manures, feeding stuffs, tanning materials, etc., accurately defined special methods of sampling are employed. The necessary information on these points is given under the individual sections.

A. Materials in Large Pieces

This class includes coal, metallurgical ores, pyrites, pyrolusite, etc., which are usually transported in ships, canal boats, or in railway waggons. In case of water-transport, the check sampling takes place as a rule at the port of arrival, during the transfer to the railway waggons, or where the factory or the foundry receives the goods at its own landing-place, samples are taken there during the unloading into trucks or other transport vessels. In other instances the sample is taken on arrival of the train at the works, either before or during the unloading of the material. In all these cases the sampling can be advantageously combined with the weighing. The taking of samples from a large heap of coarse material already unloaded is always a very uncertain procedure, and should be avoided whenever possible. Apart from the general difficulties which unavoidably occur in the conditions of sampling mentioned above, two additional difficulties arise in the last case; on the one hand, changes in the amount of moisture may occur owing to evaporation, showers of rain, downward percolation of moisture, etc., and secondly, the larger pieces are apt to roll forwards, and thus make the mass still less homogeneous than before.

The larger and the less uniform the pieces of the material in question are, the larger must be the samples taken. It is most important to secure a due ratio between the larger pieces and the finer powder, which is practically always present, since there is often an essential difference in quality between the two.

If the pieces do not exceed a billiard ball in size, and are roughly of the same dimensions, it is sufficient to take a sample from each unit-load[1] by means of a scoop of about 5 kilos (12 lbs.) capacity. If the

[1] This term designates the load raised by a crane, carried by a truck, or any other conveyance, by means of which the material is transported from the hold of the ship, etc., to the weighing machine, or to the landing-place.

material is in larger pieces, and especially if not uniform in size, it is preferable to empty a whole unit-load at intervals, *e.g.*, the tenth or twentieth load on the weighing machine, on to a separate place, from which the whole average sample is collected. The greatest possible care must be taken, in sampling by this method, to have the ratio between coarse and fine material represented as accurately as possible in the average sample.

The average sample thus obtained is first crushed to pieces about the size of a walnut, either by hand or by means of a mechanical arrangement such as studded rollers, care being taken to break down the whole of the coarse pieces, even though it may be troublesome to do so. The roughly broken material is then thoroughly mixed by repeated scooping backwards and forwards, and is then spread out in a flat heap and a smaller sample taken. This is best effected by cutting two stripes crossing each other at right angles out of the whole heap, and adding to this four smaller quantities taken from the middle of each remaining quadrant.

An alternative method is to place the material on a tiled floor, spread it out in a circle, and then, starting from the circumference, shovel it towards the centre until it is heaped up in a cone. The cone is then broken up, the material again spread out and the operation repeated. After three such mixings the evenly spread mass is divided into four quadrants, and two opposite quadrants, or one only, are taken aside, mixed and again divided.

The weight of the sample thus prepared should be at least 10-12 kilos ($\frac{1}{4}$ cwt.); if the material is very uneven in size, considerably more must be taken and special attention must be paid to the precautions described above for obtaining a true average sample. In such cases it is often necessary to repeat the above operation by scooping the first large sample together in a conical heap, spreading it out flat again, and then cutting two stripes intersecting at right angles, and adding further material from the quadrants as above.

Several mechanical samplers have been constructed in order to make this operation simpler and more reliable, such as the "rapid sampler" of P. Clarkson[1] (Fig. 1). The principle of the machine is to cut out a number of sections of the material as it passes through the apparatus in an annular rotating stream; the relative amounts can be regulated at discretion. This machine can be employed for liquids, powders, and for substances in grains or in large fragments. It is also very suitable for uniformly distributing a sample into bottles.

The reduced sample thus obtained is then further broken up. A mechanical arrangement may also be employed at this stage, but only when it is so arranged that it can be thoroughly cleaned after every

[1] For a full description, see *J. Soc. Chem. Ind.*, 1894, 13, 214.

operation. The more common practice is to effect the grinding by hand, usually in a large iron mortar. This, however, is not the best method, because it is not very easy to remove the powder completely from the mortar without loss, and the uniformity of the sample is thus adversely affected; also, some of the substance may easily remain behind unnoticed in the mortar and contaminate the next sample. (For arrangements for grinding, *cf.* p. 12.)

To overcome the disadvantages of an ordinary mortar, a flat cast-iron plate, specially constructed for the purpose, 0·8-1 metre square, with a vertical rim 5-10 cm. high, interrupted at one point in order to allow of the powder being easily run out, may be substituted; these plates should be 20-25 mm. thick, and solidly embedded in a horizontal position to prevent breakage. The sample, previously reduced to pieces not larger than walnuts, is further broken up on the plate with a sledge-hammer, shaken from time to time through a sieve of 3 mm. mesh, and the residual coarse powder repeatedly ground up until it has all passed through the sieve. In this way complete cleanliness can be observed with much greater certainty than in the use of a mortar.

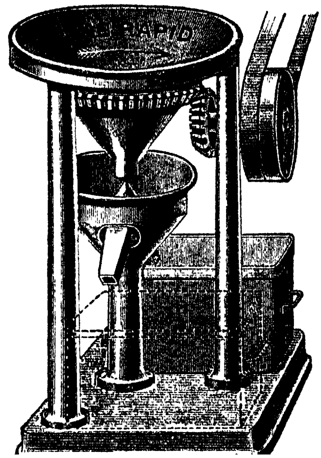


FIG. 1.

The 10-12 kilos (¼ cwt.) thus obtained is then spread out flat, and a further decreased sample of 1-2 kilos (2 to 4 lbs.) prepared from it by thorough mixing and removal of intersecting stripes, etc., in the same way as before. This is subjected to a further mixing, and the separate samples for analysis are then taken from it, preferably as follows. Three, four, or more wide-mouthed sample bottles holding 100-200 c.c. are placed close together on a sheet of paper; a handful of the sample is taken, and the hand moved over the bottles in succession, so that some of the substance falls into each. This is repeated until the bottles are quite filled. Manipulation by hand is more reliable than the use of a small scoop, etc.; with the latter the coarser particles always roll forward, so that too large a proportion is delivered into the foremost bottles.

When the bottles are full, they are closed immediately with tight-fitting corks, which are cut off straight above the necks of the bottles and carefully sealed. When control samples are taken, the seals of both parties are affixed in such a way that the cork cannot be removed without injuring the seals.

The powdering, mixing, and filling of the bottles should be carried

out as quickly as possible, to prevent the evaporation of water from moist products, or, conversely, to prevent the absorption of moisture (under special circumstances of oxygen or of carbon dioxide also) from the atmosphere.

The analyst, on receiving the sealed bottles, notes the seal, which must of course be intact, and the affixed label, opens the bottles, shakes out the contents on to glazed paper, and mixes the sample quickly. If the moisture is to be estimated, a sufficiently large sample, up to 100 g., is taken for this purpose without further grinding. The remainder is ground up until the whole passes through a sieve of 1 mm. mesh. Porcelain or steel mortars are used for the grinding, according to the hardness of the substance. The former would not be suitable for pyrites, for example, because they are attacked to some extent by substances of this degree of hardness, and the sample might be contaminated; on the other hand, iron vessels should not be used for reducing pyrolusite to a fine powder, because some metallic iron might thus find its way into the sample.

Finally, a few grams of the substance which has passed through the 1 mm. sieve are taken, after a further thorough mixing, and reduced by means of an agate mortar to the degree of fineness requisite for analysis; in special cases a steel mortar may be employed.

Since some change in the amount of moisture is almost unavoidable during the final grinding, the final sample is either dried in a drying oven or exsiccator, and then weighed out in the dry condition for analysis, or the moisture is determined separately in another sample and the results calculated on the dried substance. The actual percentage of moisture in the sample is taken from the determination made with the coarsely powdered substance as above, and not from this last determination.

B. Materials in the Form of Powder, Dross, etc.

This class includes ores in the form of smalls or slimes, common salt, potassium salts, etc., as well as many other inorganic and organic materials. A simplified method of sampling can usually be employed for such products, samples being taken from each "unit-load" by means of a scoop of about ½ kilo (1 lb.) capacity; in a railway-waggon load, several samples from different parts, *e.g.*, the front, middle, and back, are taken. The separate samples are placed together in a cask and covered over. After the sampling is finished, the contents of the cask are emptied out on a level, clean, hard surface, spread out flat, and the mass scooped together into a cone in the centre by working regularly round the heap with a spade; the heap is again spread out flat and a sample of about a quarter of the mass taken by removing two

intersecting stripes with the scoop, and adding to this some material from the middle of each of the remaining quadrants. This operation is repeated with the sample thus obtained, until finally not more than 2 kilos (4 lbs.) is left, which, after being well mixed, is divided among the sample bottles required for analysis, as described.

For materials which are loaded in loose condition, *e.g.*, in ships' holds, railway waggons, or carts, it is better to employ an *auger*, especially if the samples have to be taken from stores or from casks, boxes, or sacks. In the latter a sample is taken from every fifth, tenth, or twentieth cask or sack, according to the size of the consignment and the probability of inequality in the material; it is to be borne in mind, however, that, owing to the action of the air (or possibly owing to deceitful manipulation!), the condition of the outside and superficial portions of the material may differ more or less from that of the interior. It is, therefore, always more reliable to use the auger.

FIG. 2.

The usual form of this instrument is shown in Fig. 2. It consists of a long borer of stout sheet-iron, with a hollow interior and a longitudinal slit on one side, provided with a handle *a* at the upper end, and with the lower end beaten out to a sharp point *b*.

The use of the auger renders it possible to obtain a sample throughout the whole layer of substance. If a sample is to be taken from sacks or casks, the instrument is used only once for each vessel, but if, on the other hand, it is to be taken from a large heap stored in a warehouse or the like, the auger should be inserted in from six to twelve different places according to the size of the heap. Care must be taken to turn the instrument on its axis when it is lowered into the heaps, casks, etc., for drawing the sample.

This simple form of the auger has several defects. For example, in the sampling of sugar it is quite satisfactory for the purer primary products and even for well-separated secondary products, but it is not reliable for moist, syrupy cane sugar, because the column of sugar, on being drawn out, is apt to break off at the lower end of the auger. Consequently, according as the sack is erect or inclined, the sample may represent either the moistest part of the contents containing most syrup, or the best-drained portion. Again, in taking samples of granulated or crystal sugar, it often happens that none of the sugar remains in the sampler.

The auger designed by Gawalowski[1] avoids these drawbacks. This (Fig. 3) consists of a metal sheath which has a metal bearing suitably soldered to it at B, and in which slides a quadrangular or

[1] *Oest. Zeit. Zuckerind.*, 1888, Part V.

triangular steel rod provided with a handle (C). The valve at the lower end of the sampler is movable by means of a hinge, in such a way that in position D_1 it allows the substance to be sampled to enter from below upwards, whilst in position D it prevents the sample from falling out of A. When the auger is pushed into the material, the rod C slides sideways in such a way that the flap is fixed in position D_1, and on withdrawing it the rod C releases the flap and the latter is closed by the pressure of the substance in the sack on the attached flange.

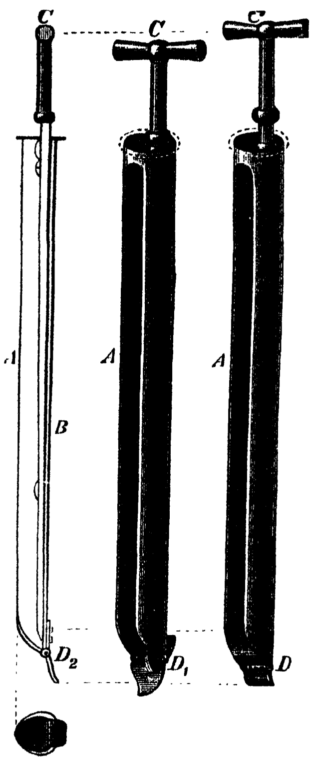


FIG. 8.

Gawalowski's auger works automatically, and samples of material can therefore be taken quickly and safely; it is made of copper or other suitable metal.

In whatever way the separate samples may have been taken, they should first be emptied into a box, or, in the case of alterable substances, into a large bottle, which must be kept corked between each addition. The whole contents of the vessel are then thrown out on to a large sheet of paper, thoroughly mixed, any lumps that may be present crushed with a spatula, and then, if the quantity is too large, a smaller average sample taken, as described above. The samples are then placed in bottles, corked and sealed.

In the case of substances which alter quickly in the air, such as bleaching powder, potassium carbonate, etc., the sample bottles must be kept well closed, and only opened when a new portion of the sample is to be added; similarly, the mixing and distribution of the sample into the bottles must be carried out as quickly as possible.

C. Liquids

The sampling of mobile liquids is a very simple operation, but that of viscous liquids, and especially of sticky, syrupy substances and pasty mixtures, is more difficult. When ordinary liquids are contained in large receptacles, the different layers very often differ in composition.

If, owing to shaking during transport, or from other circumstances, it can be taken for granted that the contents of each individual vessel are uniform, a small sample is taken from every fifth, tenth, or twentieth

cask or carboy, etc., by means of a syphon, or as otherwise desired, and an average sample prepared by mixing and shaking. The taking of samples when smaller vessels used for transport are being emptied into a larger receptacle is very simply effected, by placing a small flask, held by means of a wire (Fig. 4), under the bunghole or stopcock of the cask, or the mouth of the jar.

In large receptacles, where the different layers might vary in quality, the sample is taken by means of a glass tube of suitable length, contracted above and below, the equivalent of a pipette, which is gradually lowered into the liquid, so that a section through the whole depth of the vessel is obtained. An iron tube, provided with some kind of valve, may often be employed for this purpose.

FIG. 4.

If a sample of a very large quantity of liquid has to be taken, *e.g.*, from a tan-cistern holding 10,000-15,000 kilos (10 to 15 tons), or from a larger reservoir holding 100,000-200,000 kilos (100 to 200 tons), the sampling with the glass pipette or long iron tube provided with a valve at the lower end must be repeated several times.

Gawalowski[1] has constructed a suitable pipette for liquid and semi-liquid substances, which consists of two iron cylinders, one inside the other, closed at the lower ends, and each having a fairly wide longitudinal slit; they are so connected, by means of a bayonet-slot, that the two longitudinal slits can be made to coincide to form a single closed hollow cylinder, by a simple rotation. The instrument, which is sufficiently long to be able to penetrate all the layers of a large cask when held by the handle at the top, is introduced into the liquid in the closed position and then opened, so that liquid enters uniformly from all levels; the cylinder is then closed, withdrawn, and the contents delivered into a shallow vessel.

For taking samples of liquid intermediate products of a working process, the specific apparatus is provided with stopcocks or valves, by means of which samples can be taken as often as desired. If, however, an average sample, consisting of a number of single samples, taken seriatim without a break, is desired, so-called "dropping-bottles" are employed. These are large jars, holding about 50 litres, into which the liquid drops uninterruptedly. The rate of flow is regulated by means of a valve, and the dropping is controlled by means of a glass tube attached by a rubber connection, carrying a narrow rubber ring inside at the top, in which a small glass tube drawn out to a fine point is fixed.

[1] *Oest. chem. u. tech. Zeitschrift*, 1889, 6, 197.

Satisfactory average samples of effluents and the like can be obtained by employing a water-wheel revolving in the liquid, by means of which small samples of the liquid are continuously transferred to a reservoir, from which the average sample is taken.

Very concentrated liquids, in the analysis of which possible errors in measuring would have a considerable effect, are often not employed directly for analysis, but are first diluted (*e.g.*, 1, 10, or 20 c.c. to 100, 200, 500, or 1000 c.c.), and an aliquot part of the diluted liquid taken. In many cases, however, it is simpler to measure out such liquids with an accurate pipette, *e.g.*, a 1 c.c. pipette graduated in $\frac{1}{100}$ c.c.

D. Gases

The sampling of gases, either final products, as illuminating gas, or by-products of industrial processes, is described in the section on "Technical Gas Analysis" (pp. 230-234), and under the individual industries concerned.

II.—GENERAL LABORATORY OPERATIONS

A. Grinding of Substances

The reduction of a large average sample to a smaller one has already been discussed; the grinding is effected by very diverse methods, and is carried to very different degrees of fineness according to the nature of the substance.

For the coarse powdering of hard substances, such as ores and analogous products, iron mortars holding from 1-20 litres and upwards are suitable, provided contact with iron is not disadvantageous.

A good arrangement for grinding is shown in Fig. 5. Instead of the pestle, there is a heavy almost spherical block, carried on a pivot at the bottom of the mortar, which is moved round by a handle, and which can readily be lifted out.

For substances which form a fine dust, the twofold evil of inconvenience to the operator and loss of material is avoided by fixing a kind of sack round the rim of the mortar; the sack is contracted at the top, where it is firmly bound round the pestle; this precaution is specially to be recommended for poisonous substances.

It is almost always necessary to pass the material in the mortar through a sieve from time to time, and to powder the coarse residue separately.

For very hard ores and the like, an ore crusher can be employed with great advantage, or a set of small cast-iron rolls, the ground material

being collected in a wooden box. Malleable particles left behind on sieving pulverised ores must be kept apart, and their weight and proportion to the total weight of the sample noted.

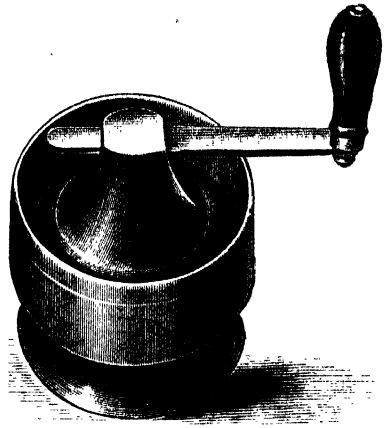


FIG. 5.

For grinding small amounts of material, the ordinary steel mortar is used; when dust is to be avoided, it is provided with a brass cover, which is screwed on.

In place of a steel mortar, a cast-iron plate can be employed, on which the sample is broken up with a heavy hammer, or a bucking plate with a heavy bucking hammer. (Fig. 6.)

Less hard substances are usually powdered in porcelain or earthenware mortars; these would give up some of their material to harder substances. Apparatus constructed on the principle of coffee-mills, and made either of earthenware or of iron, is also used.

In large works where one and the same kind of substance has often to be powdered, mechanical grinding-machines are employed, such as small ball-mills, plain, ribbed, or toothed rollers, apparatus similar to coffee-mills, or small crushers with vertical rollers.

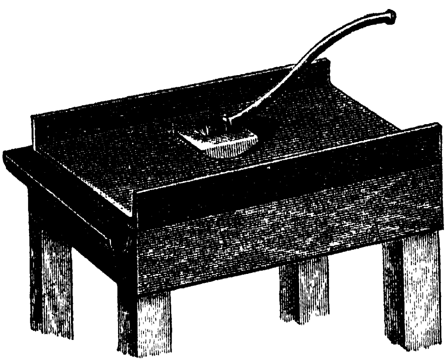


FIG. 6.

The breaking up of tough substances and of exceptionally irregular materials often requires special apparatus; these are described in the respective sections, but it may be mentioned that cutting-machines working on the lines of a hay or straw chopper, coffee-mills, toothed crushers, and the like, may often be adapted for this purpose.

All forms of grinding apparatus should be accessible in all their parts for thorough cleaning, and should be cleaned regularly.

Reduction to a fine powder for analysis is effected in agate, porcelain, or steel mortars, according to the nature of the substance, and is, as a rule, combined with rubbing ("bagging") through silk gauze.

B. WEIGHING

A laboratory balance when adjusted should give readings to within 0·1 mg.; the more delicate assay balances are subsequently discussed. The principles of weighing, calibration of weights, etc., are described in the ordinary text-books on analytical chemistry. Rough balances, usually without a glass case, are used for weighing out large amounts of substance. For many purposes an intermediate quality of balance, reading to 1 mg., and provided with a glass case, is very convenient, particularly for weighing out fairly large quantities of material, which are then dissolved and made up to a definite volume, of which an aliquot part is taken for the analysis.

For less accurate work, druggist's hand-scales, with horn scale pans suspended by silk cords, are very useful, the substance being weighed directly into the scale pan. A handy form of this balance is shown in Fig. 7. One arm is graduated in 100 divisions and provided with a sliding weight, so that from hundredths of a gram up to 1 gram can be weighed out directly, whilst larger quantities are balanced by ordinary weights placed in the scale pan.

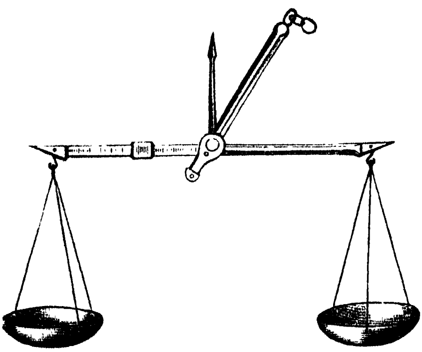


FIG. 7.

These hand-scales are usually only employed for loads up to 30 g. and to an accuracy of 10 mg.; they are also made to carry 100 g. and over.

For calibrating litre flasks, and for many other purposes, a balance is required which can be loaded up to 2 kilos and turns with 50 mg.; it can be used for many other analytical purposes also, *e.g.*, in the estimation of moisture in coal, coke, salt, etc., where 100 g. or more of substance is weighed out. No matter what kind of balance is employed, the greatest possible rapidity in weighing is always to be aimed at; the necessarily numerous daily analyses cannot possibly be made if five or ten minutes are taken up for each weighing.

Many simple artifices are accordingly used. In weighing on sensitive balances, crucibles, watch-glasses, beakers, etc., the weight of which is known to 1-2 mg., are used, and this weight is written either on the glass itself, or the vessels are marked with successive numbers, and a note of the weights corresponding to the individual numbers recorded. In the weighing of platinum crucibles, etc., which are in frequent use, the actual weighing is really only a check, involving a correction of the weight within the limits of a few mg.

If one and the same vessel is very frequently used in weighing, it is very convenient to cut a tare for it out of copper, nickel, or aluminium foil, which is placed in the other scale pan. With suitable precautions this procedure, which saves much time, may be employed in weighing platinum crucibles for gravimetric analysis.

In works' laboratories it is exceedingly convenient to have a single weight, made of aluminium, lead or nickel foil, and adjusted by filing down, as the tare for any very frequently occurring quantities, and on which the required weight is clearly marked.

The weighing out of exactly 0·5, 1, 2, 5, 10, 20, 50 g., etc., has the advantage that the analytical results are easily calculated to percentages; this method can be much recommended, and has been generally introduced in works' laboratories.

Another very useful method of weighing which is often employed in technical laboratories is to weigh out such an amount of substance (or, in certain circumstances, a multiple of the amount) that the number of c.c. of volumetric solution used, or, in gas volumetric analysis, the volume of gas evolved, gives a percentage value either without any calculation or by a simple mental multiplication or division. For example, in the analysis of bleaching powder the "available" chlorine is required; Penot's arsenious acid solution is made up to correspond to 0·1 g. molecules, or 3·546 g. chlorine per litre, or 0·003545 g. per c.c. Consequently, $20 \times 0{\cdot}3546$ g. $= 7{\cdot}092$ g. bleaching powder are dissolved in a litre, and 50 c.c. = 0·3546 g. taken for a titration; then each c.c. of the solution indicates 1 per cent. of available chlorine. For the estimation of calcium carbonate in a sample of limestone by measurement of the evolved gas, since 1 c.c. carbon dioxide at 0° and 760 mm. weighs 1·9768 mg., this corresponds to 4·497 mg. calcium carbonate; accordingly 0·2248 g. of the limestone is weighed out, so that each c.c. of carbon dioxide obtained corresponds to 2 per cent. of calcium carbonate in the sample.

The correction of weighings for the buoyancy of the air can be neglected in general technical work, as the errors involved are inappreciable in their relation to the methods of experiment and manipulation employed.

C. Solution. Evaporation

The substance can often be weighed directly into the vessel in which it is to be dissolved; this saves time, and avoids the possibility of loss during transference from the weighing bottle to the vessel employed for the solution. It is, however, very important to select a vessel that completely fulfils its purpose, even if such direct weighing is thereby prevented.

The vessels chosen should in almost all cases be adapted for heating; if this is the only consideration, beakers, porcelain basins, etc., suffice, but if there is any risk of loss from spirting, suitable precautions are necessary. The employment of very large basins or beakers as a means of avoiding loss from this cause is deceptive, and leads in other respects to both inconvenience and inaccuracy. Such operations should be carried out in narrow beakers or in Erlenmeyer flasks, which are kept covered during the process, either by clock-glasses bored through the middle, or by funnels cut off at the neck (Fig. 8), and which are subsequently washed both inside and outside with a few drops of water.

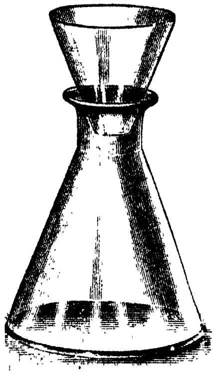


FIG. 8.

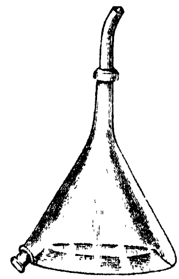


FIG. 9.

When there is not much liquid to evaporate off, the evaporation is best carried out in the vessel used for solution, especially when previous filtration is not necessary, and a precipitation, etc., is to be effected in the same vessel. With larger amounts of liquid, and especially if concentration at the boiling-point is too rapid, vessels with a large surface area, such as basins, are employed, covered preferably by a funnel of the form shown in Fig. 9.

D. PRECIPITATION, FILTRATION, AND WASHING OF PRECIPITATES

Regarding precipitation, there is little to add to what is known from general analysis. In works' laboratories it is usual, and quite rightly so, not to be so scrupulous about the long standing after precipitation and before filtration as is often customary in scientific laboratories. Accurate investigations led long ago to the conclusion that even where formerly it was recommended to allow a precipitate to stand twelve to twenty-four hours, quite as good results are obtained if the liquid is allowed to clear, which it does after from half an hour to two hours, and then filtered immediately. For instance, in the determination of phosphoric acid by molybdic acid, in the precipitation of sulphuric acid by barium chloride, and even in the precipitation of phosphoric acid by magnesia mixture, etc., prolonged standing is unnecessary if definite conditions are observed; in the precipitation of sulphuric acid, for example, the solution must be kept boiling briskly, and the barium chloride added hot, without interrupting the boiling, in order that the precipitate may form in a granular condition. In other cases the

solution must be continually stirred during precipitation; this is now much facilitated by the use of mechanical stirrers.

It is very convenient to prepare reagents in solutions of definite strength, as it expedites the work very greatly if it is known beforehand how much of a solution is required for a precipitation or any other reaction. It is naturally very important not to add too small an amount of the precipitant, but an excess may also be deleterious if the reagent is carried down by the precipitate (as is the case with barium chloride in presence of barium sulphate), or if the latter is soluble in an excess of the former, etc. This is avoided by the use of solutions of known strength, and by always taking the same or approximately the same weight of substance for analysis; a definite, measured volume of the reagent, sufficient for complete precipitation but not very greatly in excess, is added. In this way a single control test suffices, instead of having possibly to make a number of check tests.

To avoid the filtration and washing of a precipitate, when the filtrate only is required for further investigation, a method frequently adopted in technical laboratories consists in making up the liquid to a certain volume and withdrawing an aliquot part with a pipette, or, as an alternative, pouring it through a dry filter paper. This plan expedites the work very much, but it is to be borne in mind that a certain error arises, owing to the volume occupied by the precipitate, which must be taken into account in accurate work, and also that more of the soluble constituents is frequently retained, owing to adsorption, etc., than corresponds to the interstices of the precipitate. Further, the filter paper may remove certain constituents from the liquid by adsorption; in such cases filtration must be omitted, and the clear liquid separated from the precipitate by careful decantation. If the solution is acted upon by the air, it must be withdrawn directly from the graduated flask containing the precipitate.

The funnels selected for filtration must be of the right angle (60°), so that the filter paper can be accurately fitted, otherwise the liquid passes through too slowly; filter papers should be of close texture, and allow of rapid filtration. For analytical purposes, cut filter papers rendered ash-free by treatment with hydrochloric and hydrofluoric acids are now almost exclusively employed; pleated filter papers are not to be recommended, even for technical laboratories, on account of the very great difficulty in washing them out, except when no washing is necessary, as, *e.g.*, if the liquid has been made up to a definite volume and an aliquot part of the clear solution is to be employed for analysis.

Filter pumps are not generally used in technical laboratories except when the precipitates are particularly difficult to deal with; this is because a large number of filtrations are usually carried on simul-

taneously, and the various plans to avoid the tearing of the filter paper are too troublesome under these conditions.

The Gooch crucible (Fig. 10) is now advantageously used instead of the ordinary funnel in many cases. It is made either of porcelain or platinum, and has the bottom perforated by a number of small holes; if the precipitate has to be ignited as well as dried, as in platinum determinations, the crucible is fitted with a smooth dish-shaped tray. An asbestos filter is constructed on the perforated base of the crucible by first introducing a layer of asbestos in long fibres and then short fibre asbestos, both of which have been previously washed with concentrated hydrochloric acid and subsequently with water; a perforated plate of platinum or porcelain is placed over the asbestos, and more fine fibre asbestos above the plate. The crucible *a* is fixed in an adapter *b* by means of a thin-walled wide rubber tube, and the neck of the adapter inserted in the neck of a filter flask *c*, to which a filter pump can be applied at *d*. Distilled water is first passed through to wash away any loose threads of asbestos, the crucible is then taken out, dried under the same conditions as are subsequently adopted with the precipitate, and weighed; the filtration is then carried out as with an ordinary funnel, the precipitate being collected on the layer of asbestos. After filtering and washing, the crucible is again placed in the drying oven, and dried at the desired temperature; if it is necessary to heat over a free flame, the crucible is placed inside a larger crucible and heated, at first gently, and then at the desired temperature. Many estimations can be carried out successively with the same filling of asbestos, especially if the upper part of the contents of the crucible is removed without injuring the asbestos filter.

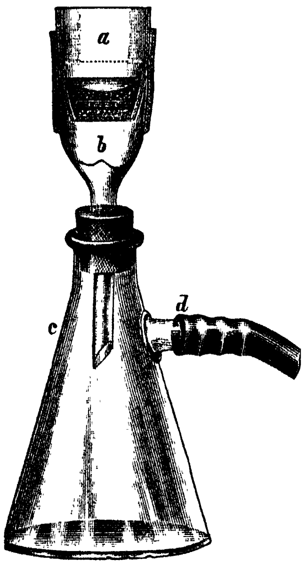


Fig. 10.

In place of the asbestos packing C. E. Munro[1] has proposed the use of platinum sponge packed in the form of a felt into a perforated platinum crucible. This possesses several advantages over asbestos. It is considerably more porous and retains satisfactorily the finest precipitates, such as barium sulphate and calcium oxalate, and further allows of the removal of the precipitate by means of suitable solvents, a list of which has been prepared by O. D. Swett.[2]

[1] *J. Anal. and Applied Chem.*, 1888, **2**, 241. *Cf.* also W. O. Snelling, *J. Amer. Chem. Soc.*, 1909, **31**, 456.

[2] *J. Amer. Chem. Soc.*, 1909 **31**, 928.

The crucible is prepared for use by placing it on several layers of filter paper and then pouring in ammonium chloroplatinate made into a paste with alcohol. The alcohol is drawn off by the filter paper, leaving behind a layer of ammonium chloroplatinate, which is first gently warmed to remove adhering alcohol and then gently ignited until completely decomposed, when a uniform layer of platinum sponge is left behind in the form of a felt. By rubbing the felt gently with a glass rod during the ignition it can be smoothed and shaped to the crucible; at the same time the deposit is somewhat compressed and burnished. If the deposit is unsatisfactory the felt should be saturated again with a solution of chloroplatinic acid, then placed in a concentrated solution of ammonium chloride and again ignited.

O. Brunck[1] has devised a porcelain crucible for use with a platinum packing in which the felt is burned into the glaze.

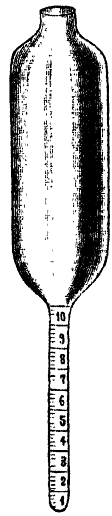


FIG. 11.

Filtration of the precipitate is avoided by the use of centrifugation, which saves both drying and igniting, and thus leads to a great saving of time, but the method is only applicable in quite special cases. The precipitations are carried out in vessels of the form represented in Fig. 11, which have at the bottom a narrow tube closed at the lower end, on which an empirically constructed scale is etched, which shows the volume occupied by the precipitate of a definite substance for a definite unit of weight when the precipitate is reduced to the smallest possible volume by means of centrifugal force. The scale shows either the weight of the precipitate in mg., or directly the percentage of the constituent sought, when a definite amount of the original substance is employed; the precipitation is effected in the vessel itself, and the measurement is made whilst the precipitate remains in contact with the liquid.

The centrifugal method has been applied to the estimation of phosphorus, more especially in iron and steel, the precipitate of phosphomolybdic acid being measured, to the determination of urinary deposits, of cellulose in food-stuffs, etc., and to a still greater extent to the estimation of fat in milk, of water in butter, and to the rapid separation of liquids containing bacilli and the like; tubes of different construction to the above are used for these latter purposes.

An automatic machine for the washing of precipitates has been devised by E. Sinkinson.[2] It is constructed on the principle of the rocking arm, and is actuated by a motor which is so arranged that the flow of water used for washing is automatically controlled as the funnel is filled and emptied.

[1] *Chem. Zeit.*, 1909, 33, 649.

[2] *Analyst*, 1920, 45, 94.

III.—VOLUMETRIC ANALYSIS[1]

Volumetric analysis includes "titration analysis" or volumetric analysis in the restricted sense, which consists in the application of standard solutions to the analysis of liquid and solid substances, gas-volumetric analysis, which consists in the valuation of a liquid or solid by the measurement of an evolved gas, and gas analysis. These three branches of volumetric analysis are all very extensively employed both for scientific as well as for technical work. Many of the methods are equally serviceable for both purposes, whilst others have been specially worked out for technical analysis. The latter are described in connection with the respective industries; a special section is devoted to technical gas analysis.

The Calibration and Standardisation of apparatus used in volumetric analysis.

In all branches of volumetric analysis it is of primary importance that the vessels employed should be accurately graduated.

The calibration of volumetric apparatus used in the analysis of products which are bought or sold should on no account be omitted; less accurate apparatus suffices for use in the control of working processes, but this should at least be submitted to a comparative standardisation if not actually calibrated. Apparatus for volumetric analysis can now be bought which has been tested and stamped by the National Physical Laboratory or by the Bureau of Standards of the Department of Commerce, Washington.

The conceptions as to what is to be understood by standardised vessels and what is to be required of them are very varied, and in some respects obscure.

In the first place, the unit taken as a basis for the standardisation must be clearly defined. From the scientific standpoint the litre is the space which one kilo of water, weighed in a vacuum, occupies at its maximum density and under standard pressure. Originally it was intended that a kilogram should be the mass of 1000 c.c. of water at the temperature of its maximum density, and accordingly the litre would have been 1000 c.c. in volume. The most recent determinations have shown that this is not the case, and that one litre, as defined, is equivalent to 1000·027 c.c. There is therefore a very slight difference between the c.c. and the thousandth part of a litre; this is, however, so small that it is negligible for nearly all purposes.

[1] For the history of the subject, *cf.* L. L. de Koninck, *Historique de la méthode titrimétrique*, published by Havrez, Brussels, 1901; and, *Bull. de l'Assoc. Belge de Chimistes*, 1901, 15, November and December.

Since the maximum density of water corresponds to a temperature of 4°, calibrations must either be always carried out at this temperature, which is naturally not practicable, or at a suitable higher temperature to be definitely determined, the corrections to be made being ascertained either by calculation or from tables. This is essential in order to ascertain the value of the "true litre" and its subdivisions, regard being had to the temperature of the water and the buoyancy of the air, which depends on the temperature, the pressure, and the degree of moisture present. In order to avoid the calculations necessitated by the employment of the true litre, Mohr, as early as 1855, introduced as the unit the volume which 1000 g. of water occupies when weighed in air with brass weights at 14° R. = 17°·5 C. This value is called "Mohr's litre"; it is equivalent to 1002·3 true c.c., and one true litre is equivalent to 997·7 "Mohr's" c.c. at a pressure of 760 mm.

The designation is also extended to the use of other temperatures (15°, 20°, or higher). In verifications undertaken at the National Physical Laboratory the Mohr's litre is referred to weighings in air at the standard temperature of the vessel, under a pressure of 760 mm., having a mean content of moisture and carbon dioxide. The density of the brass weights used is taken as 8·4. On this basis, for a standard temperature of 15° C., the volume corresponding with 1000 g. is 1001·980 c.c.

In view of the necessary corrections for temperature and pressure, the advantages which Mohr and his successors claimed for the choice of an alternative to the true litre disappear. The use of tables (p. 33) cannot be avoided, and the true litre in conjunction with tables (pp. 23 to 24) is, therefore, just as easily employed. It is, accordingly, very desirable that the word "litre" and its subdivisions should be restricted to the true (metric) litre, and that all chemical measuring vessels should be based upon it. The tables given below can also, of course, be used to determine the deviations of vessels graduated on Mohr's system from true litre measures.

The calibration of measuring flasks should always be carried out with the same kind of liquid as that with which they are to be filled when in use, so that the conditions of wetting, the meniscus correction, etc., are similar; apparatus to be used with mercury should always be calibrated with mercury, whilst burettes, pipettes, and measuring flasks are calibrated with water, which does not differ essentially in its behaviour from the very dilute volumetric solutions generally used in these vessels.

To avoid all the errors mentioned above, the only means is the employment of the true litre; as already stated, this is the volume which 1 kilo of water at 4° occupies under standard pressure. If this space is to be marked off, *e.g.*, on a flask, the position of the mark will

depend on the temperature of the flask. The standard temperature to which certificates are used by the National Physical Laboratory is usually 15° C.; thus the statement that the volume of a one-litre flask is correct means that at a temperature of 15° the volume of the contents of the flask is the same as that of a kilo of water at a temperature of 4°. The tables given below allow the adjustment to be made directly at any desired temperature and pressure, the weights that must be placed on the scale pan to effect this being given in each case.

Two true litre measures of glass, adjusted at different temperatures, differ only by the difference in the expansion of glass between the two temperatures, if water of the same temperature has been used in testing them. Therefore it is only necessary to calculate the weight which is in equilibrium with the weight of water occupying a true litre measure for one normal temperature, *e.g.*, 15°. If the temperature of the air does not greatly deviate from this, and the height of the barometer is not very far from 760 mm., mean assumptions may be made for the factors which influence the buoyancy of the air, pressure, temperature, and degree of moisture, and the reductions thus obtained may be combined with those due to the temperature of the water. The values in Table I. (p. 23) can then be employed directly in order to find how the volume of a true litre should be marked off on a flask. If, for example, the air and the water have a temperature of 17°, the empty flask along with a kilogram weight is placed on one scale pan and brought to equilibrium by a tare on the other; the kilogram weight is then removed, and on the same side (that is, along with the flask) weights to the amount of 2·208 g. are placed; equilibrium is then re-established by filling the flask with water at 17°, and the volume occupied by this weight of water marked on the neck of the flask.

In the case of greater deviations of the temperature of the air from 15°, and of the atmospheric pressure from 760 mm., Table II. (p. 24) is used to correct the values of Table I. If, *e.g.*, the height of the barometer is 720 mm., the temperature of the air 25°, that of the water 24°·3, the weight to be added for a litre is :—

From Table I.	3564	mg.
From Table II.	−92	mg.
	3472	mg.

The weight of the volume of water required to correspond to a true litre for the flask at 15° is therefore $1000 - 3{\cdot}472 = 966{\cdot}528$ g.

For any other normal temperature (t) the magnitude $(t-15)\ 0{\cdot}000027$ must be added to the above; thus for a normal temperature of 20° all the values of Table I. must be increased by $1000\ (20-15)\ 0{\cdot}000027 = 135$ mg. For a water temperature of 20°, $2699 + 135 = 2834$ mg. must therefore be added.

TABLE I.

Weight in mg. to be added for 1000 c.c.; the cubic coefficient of expansion of glass = 0·000027 per 0° C. Normal temperature, 15°. Water temperature, from 5°-30°·9. Height of barometer, 760 mm. Temperature of the air, 15°. Mean pressure of aqueous vapour = 8 mg. per litre.

Temp.	0	·1	·2	·3	·4	·5	·6	·7	·8	·9	Temp.
5	1341	1340	1339	1338	1338	1338	1338	1338	1338	1338	5
6	1338	1339	1340	1341	1342	1343	1344	1345	1346	1348	6
7	1350	1352	1354	1356	1358	1360	1363	1366	1369	1372	7
8	1376	1380	1384	1388	1392	1396	1400	1404	1408	1412	8
9	1417	1421	1426	1431	1436	1442	1447	1452	1458	1464	9
10	1471	1477	1483	1489	1496	1503	1510	1517	1524	1531	10
11	1539	1547	1555	1563	1571	1579	1587	1595	1603	1611	11
12	1619	1628	1637	1646	1655	1664	1673	1683	1693	1703	12
13	1713	1723	1733	1743	1753	1764	1775	1786	1797	1808	13
14	1819	1830	1841	1853	1865	1877	1889	1901	1913	1925	14
15	1937	1949	1962	1975	1988	2001	2014	2027	2040	2053	15
16	2066	2080	2094	2108	2122	2136	2150	2164	2178	2193	16
17	2208	2223	2238	2253	2268	2283	2298	2313	2328	2344	17
18	2360	2376	2392	2408	2424	2440	2457	2474	2491	2508	18
19	2525	2542	2559	2576	2593	2610	2627	2645	2663	2681	19
20	2699	2717	2735	2753	2771	2789	2807	2826	2845	2864	20
21	2883	2902	2921	2940	2959	2978	2998	3018	3038	3058	21
22	3078	3098	3118	3138	3158	3178	3199	3220	3241	3262	22
23	3283	3304	3325	3346	3367	3388	3410	3432	3454	3476	23
24	3498	3520	3542	3564	3586	3609	3632	3655	3678	3701	24
25	3724	3747	3770	3793	3816	3839	3862	3886	3910	3934	25
26	3958	3982	4006	4030	4054	4078	4102	4127	4152	4177	26
27	4202	4227	4252	4277	4302	4327	4352	4377	4403	4429	27
28	4455	4481	4507	4533	4559	4585	4611	4637	4663	4689	28
29	4716	4743	4770	4797	4824	4851	4878	4905	4932	4959	29
30	4987	5014	5041	5069	5097	5125	5153	5181	5210	5239	30

TABLE II.

Correction of the values in TABLE I. in mg. for 1000 c.c. for atmospheric pressure, 650-790 mm., and temperature of the air, 5°-31° C.

Mm.	650.	660.	670.	680.	690.	700.	710.	720.	730.	740.	750.	760.	770.	780.	790.	Mm.
Temp. 5°	−121	−106	−91	−77	−62	−47	−32	−18	−3	+11	+26	+41	+55	+70	+84	Temp. 5°
6	124	109	95	80	66	51	36	22	7	+7	+22	37	51	66	80	6
7	128	113	99	84	70	55	40	26	11	+3	+18	32	47	61	76	7
8	131	116	102	87	73	58	44	29	15	0	+14	28	43	57	72	8
9	135	120	106	91	77	62	48	33	19	−4	+10	24	38	53	67	9
10	138	124	109	95	80	66	52	37	23	8	+6	20	34	49	63	10
11	−141	−127	−112	−98	−84	−70	−56	−41	−27	−12	+2	+16	+30	+45	+59	11
12	145	131	116	102	88	74	60	45	31	16	−2	+12	26	41	55	12
13	148	134	119	105	91	77	63	49	34	20	−6	+8	22	36	50	13
14	152	138	123	108	94	81	67	53	38	24	−10	+4	18	32	46	14
15	155	141	127	112	98	85	71	57	42	28	−14	0	14	28	42	15
16	−158	−144	−130	−116	−102	−88	−74	−60	−46	−32	−18	−4	+10	+24	+38	16
17	161	147	133	120	106	92	78	64	50	36	22	−8	+6	+20	34	17
18	165	151	137	123	109	95	81	67	53	39	25	−11	+3	+16	30	18
19	168	154	140	127	113	99	85	71	57	43	29	−15	−1	+12	26	19
20	171	157	143	130	116	102	88	74	61	47	33	−19	−5	+8	22	20
21	−174	−161	−147	−133	−119	−105	−91	−78	−64	−51	−37	−23	−9	+4	+18	21
22	177	164	150	137	123	109	95	81	68	54	40	26	−13	+1	+14	22
23	181	167	154	140	126	112	98	85	71	58	44	30	16	−3	+11	23
24	184	171	157	144	130	116	102	88	75	61	47	33	20	−6	+7	24
25	187	174	160	147	133	119	105	92	78	65	51	37	24	−10	+3	25
26	−190	−177	−163	−150	−136	−122	−109	−95	−82	−68	−55	−41	−28	−14	−1	26
27	193	180	166	153	139	125	112	98	85	71	58	45	31	18	4	27
28	197	184	170	157	143	129	116	102	89	75	62	48	35	21	8	28
29	200	187	173	160	146	132	119	105	92	78	65	52	38	25	11	29
30	203	190	176	163	149	135	122	109	95	82	69	56	42	29	15	30
31	−206	193	179	166	152	138	125	112	99	86	73	60	46	33	19	31

If a different value to the above be chosen for the mean expansion coefficient of glass, then $1000 (a' - 0{\cdot}000027)(t - 15)$ must be added to the values of Table I., a' denoting the new coefficient of expansion of glass, and t the temperature of the water. The amount of this correction is always very small, and is hardly likely to be employed by the chemist in calibrating.

The Tables I. and II., pp. 23 and 24, were calculated by W. Schloesser.[1]

The following methods and conditions are adopted by the National Physical Laboratory for the testing and calibration of scientific glassware.[2]

The tests are divided into the two groups of **Class A Tests** which are applicable to the examination of vessels of the highest accuracy, and **Class B Tests** for vessels intended to possess only commercial accuracy.

In the case of both tests certain conditions are laid down in respect to cleaning, construction, inscription and graduation marks of all vessels submitted for verification.

The general methods of testing are as follows :—

(1) When apparatus is received for test, it is first examined to see if the conditions specified are complied with. If intended for delivery through a jet, the time of delivery is determined.

If found to be satisfactory in these respects, the capacity test is proceeded with. If the apparatus does not fulfil the above conditions no further examination is made, and the apparatus is returned to the sender.

(2) In the majority of cases the volumes are determined by weighing the quantity of pure distilled water which the vessel contains (or delivers). The temperature of the water, the temperature of the surrounding air, and the barometer reading are also noted. On the basis of these observations the true volume of the vessel at its standard temperature is calculated.

(3) Vessels for use with mercury are tested with this liquid, using, when possible, a rising meniscus. The weight of their mercury content is determined, and the required volume is deduced from the results obtained, the temperature of the mercury at the time of test and the buoyancy effect of the air being taken into account.

(4) The adjustment of a water meniscus to a mark on a vessel is made so that the lowest point of the meniscus is in the plane which contains the mark. In this adjustment the axis of the vessel should be

[1] *Z. angew. Chem.*, 1903, **16**, 953, 977, and 1904 ; *Chem. Zeit.*, 1909, **25**, 509.

[2] The authors are indebted to Sir J. E. Petavel, Director of the National Physical Laboratory, Teddington, Middlesex, for these data. A pamphlet containing full details of the tests, certificates issued, and charges is published by the Laboratory.

vertical, and the observer's eye placed in such a position that the front and back halves of the mark coincide. The meniscus should be shaded by folding a strip of black paper round the vessel, the top edge of which should not be more than 1 mm. below the mark on which the setting is to be made. The meniscus so shaded should be viewed against a white background.

(5) In the case of vessels which are intended for use with mercury the upper surface of the meniscus is brought into coincidence with the mark. The mercury surface should be shaded by a strip of black paper placed just above the mark to which the meniscus is to be set, and viewed against a white background.

(6) Vessels calibrated for delivery and provided with lips, are emptied into a glass by gradually inclining them, until, when the continuous stream of the liquid has ceased, they are nearly vertical. In this position they are allowed to drain for half a minute, and the lip is then stroked against the glass.

Flasks intended for delivery are emptied in a similar manner.

(7) Graduated vessels are ordinarily tested at five points.

The following data are included in the detailed regulations and tolerances specified by the laboratory.

Class A Tests

Flasks.

(1) In the verification of a flask, the vessel is first carefully cleaned, and filled with distilled water to a few millimetres above the mark, care being taken to avoid wetting the neck above this level. The surface is then adjusted to the mark by removing small quantities of water with a fine capillary tube.

(2) The inner diameter of the neck at the mark must not exceed the values given below:—

Capacity c.c. .	10	25	50	100	250	500	1000	1500	2000	3000	4000	5000
Diameter mm.	6	8	10	12	14	16	18	20	25	30	35	40

(3) The *Class A* tolerances allowed on flasks are :-

Capacity c.c. .	10	25	50	100	250	500	1000	1500	2000	3000	4000	5000
Tolerance $\pm$ c.c. for content .	0·008	0·015	0·03	0·05	0·08	0·15	0·20	0·25	0·35	0·5	0·8	1·0
for delivery .	0·016	0·03	0·06	0·10	0·16	0·30	0·40	0·50	0·70	1·0	1·6	2·0

Pipettes.

(1) The outlet must be of such a size that the time occupied by the outflow of water, as defined in paragraph (3) below, conforms with the times given in the following table:—

Capacity c.c.	2	5	10	50	100	250	500
Minimum delivery time allowed: secs. .	5	10	15	20	30	45	60
Maximum delivery time allowed: secs. .	10	20	30	40	60	90	120

(2) The time of outflow and the drainage time (15 secs.) must be marked on all pipettes. The actual time of outflow must be within the limits given in the preceding paragraph, and also must not differ from the time etched on the pipette by more than the amounts given in the following table:—

Marked time of outflow: secs.. . . .	30	60	90	120
Maximum difference allowed between the marked time of outflow and the actual time of outflow ± secs.	2	4	6	8

NOTE.—For marked times of outflow not given in the above table, the tolerances are the same as for the next larger tabulated times.

(3) Ordinary pipettes are clamped vertically for test, and filled with water to a short distance above the mark. Water is run out until the meniscus is on the mark and the outflow is then stopped. The drop adhering to the tip is removed by bringing the surface of some water contained in a beaker into contact with the tip and then removing it without jerking. The pipette is then allowed to deliver into a clean weighed vessel held slightly inclined so that the tip of the pipette is in contact with the side of the vessel. The pipette is allowed to drain for ¼ minute after outflow has ceased, the tip still being in contact with the side of the vessel. At the end of the draining time the receiving vessel is removed from contact with the tip of the pipette, thus removing any drop adhering to the outside of the pipette. To determine the instant at which the outflow ceases, the motion of the water surface down the delivery tube of the pipette is observed, and the delivery time is considered to be complete when the meniscus comes to rest slightly above the end of the delivery tube. The ¼ minute draining time is counted from this moment.

(4) The *Class A* tolerances allowed on pipettes are:—

Capacity c.c. . . .	**2**	**5**	**10**	**20**	**30**	**50**	**100**	**150**	**250**	**500**
Tolerance ± c.c. for content or delivery	**0·006**	**0·01**	**0·015**	**0·02**	**0·025**	**0·035**	**0·05**	**0·07**	**0·08**	**0·15**

Burettes and Graduated Pipettes.

(1) Enamel-back burettes are not admitted to Class A tests. Burettes without taps are also excluded.

(2) The graduated portion of graduated pipettes must not exceed 35 cms. in length.

(3) The diameter of the outlet must be of such a size that the time occupied by the outflow of water from the zero mark to the lowest graduation mark conforms with the *Class A* limits given below.

Length Graduated : cms.	15	20	25	30	35	40	45	50	55	60	65	70	75
Minimum Time of Outflow : secs.	30	40	50	60	70	80	90	100	110	120	130	140	150
Maximum Time of Outflow : secs.	60	80	100	120	140	160	180	200	220	240	260	280	300

NOTE.—(*a*) For lengths not tabulated, the times allowed are those corresponding to the next larger tabulated length.

(*b*) The time of outflow of burettes is taken with the stopcock fully open.

(4) The time of outflow must be marked on the tubes of all burettes and graduated pipettes. The actual time of outflow must be within the limits given in the preceding paragraph, and also must not differ from the time marked on the instrument by more than the amounts given in the following table:—

Marked time of outflow : secs.	50	100	150	200	300
Minimum difference allowed between the marked time of outflow and the actual time of outflow ± secs.	4	8	12	16	20

NOTE.—For marked times of outflow not given in the above table, the tolerances are the same as for the next larger tabulated times.

(5) Burettes and graduated pipettes are clamped vertically for test, and filled with water to a short distance above the zero mark. Water is then slowly run out until the meniscus is exactly on the zero mark. The drop adhering to the tip is then removed by bringing the tip into contact with the inside of a glass beaker. The instrument is then allowed to deliver freely, *i.e.*, in the case of burettes, with the stopcock fully open, into a clean weighed vessel. It is necessary, however, to arrest the full flow of liquid in time to obtain control over the final movement of the water surface and to bring the meniscus to rest accurately on the line to be tested. The instrument is therefore allowed to deliver freely until the water surface is approximately 1 cm. from the

line to be tested. The rate of outflow is then reduced and the motion of the water surface brought under control so that an accurate setting can be made on the line in question. No period of waiting for drainage is allowed. The drop adhering to the tip after the setting has been made is removed by bringing the side of the receiving vessel into contact with the tip.

(6) The zero mark is always taken as the starting-point of the intervals tested.

(7) The *Class A* tolerances allowed on burettes and graduated pipettes are:—

Total capacity c.c.	2	10	30	50	75	100	200
Maximum error allowed at any point, and also maximum difference allowed between the errors at any two points for content or delivery ± c.c.	0·01	0·02	0·03	0·04	0·06	0·08	0·15

NOTE.—(*a*) For capacities not tabulated, the tolerances are the same as those given for the next larger tabulated capacity.

(*b*) The tolerances apply to the whole of the graduated portion and to any fraction of it. Thus, for example, a 50 c.c. burette may be in error by ±0·04 c.c. at any point provided that the difference between the errors at any two points tested does not exceed 0·04 c.c.

Graduated Cylinders.

(1) Graduated cylinders calibrated for "delivery" are not admitted to Class A tests.

(2) The graduations should be omitted from the bottom portion of the cylinders for a length corresponding to one-tenth of the nominal capacity. Thus, for example, the graduations on a 500 c.c. cylinder should commence at the 50 c.c. mark, and below this point the cylinder should be left plain.

(3) The *Class A* tolerances allowed on graduated cylinders are:—

Total capacity c.c.	5	10	25	50	100	250	500	1000	2000
Maximum error allowed at any point, and also maximum difference allowed between the errors at any two points for content ± c.c.	0·04	0·06	0·10	0·15	0·25	0·50	1·0	1·5	2·5

NOTE.—The notes (*a*) and (*b*), relating to tolerance on burettes, apply also to graduated cylinders.

CLASS B TESTS

The conditions and methods of test for this class are, generally speaking, identical with those for Class A tests except that, in some

cases, the capacity may be determined by volumetric methods instead of by weighing.

The tolerances allowed are as follows :—

Flasks.

Capacity c.c.	10	25	50	100	250	500	1000	1500	2000	3000	4000	5000
Tolerance ± c.c. for content	0·02	0·03	0·06	0·10	0·15	0·25	0·3	0·4	0·6	0·8	1·2	1·5
for delivery	0·04	0·06	0·12	0·2	0·3	0·5	0·6	0·8	1·2	1·6	2·4	3·0

Pipettes.

Capacity c.c.	2	5	10	20	30	50	100	150	250	500
Tolerance ± c.c. for content or delivery	0·012	0·02	0·03	0·035	0·045	0·06	0·08	0·10	0·12	0·25

Burettes and Graduated Pipettes.

Enamel back burettes and burettes without taps, though excluded from Class A tests, are admitted to Class B tests.

Total capacity c.c.	2	10	30	50	75	100	200
Maximum error allowed at any point, and also maximum difference allowed between the errors at any two points ± c.c.	0·015	0·035	0·05	0·07	0·10	0·14	0·25

Graduated Cylinders.

Graduated cylinders calibrated either for "content" or "delivery" are admitted to Class B tests.

Total capacity c.c.	5	10	25	50	100	250	500	1000	2000
Maximum error allowed at any point, and also maximum difference allowed between the errors at any two points. for content ± c.c.	0·06	0·10	0·15	0·25	0·40	0·8	1·5	2·5	4·0
for delivery ± c.c.	0·08	0·12	0·20	0·30	0·50	1·0	2·0	3·0	5·0

Corresponding tests for vessels for gas analysis, vessels with auxiliary graduations, specific gravity bottles and tubes and vessels for milk analysis are also specified and verified by the National Physical Laboratory.

The methods of verification adopted in the United States are described in Circular No. 9, published by the Bureau of Standards of the Department of Commerce, Washington, in 1915.

Should it be desirable for some special reason to undertake the calibration of apparatus, this can be done with sufficient accuracy, and within the official limits of error, by employing a sufficiently stable balance, turning with 0·05 g., for vessels holding up to 500 c.c., and an ordinary analytical balance and a weighing bottle, provided with a glass stopper, for smaller vessels. The temperature of the water employed in calibrating should be determined with an accurate thermometer to within ± 0·1°.

The contents of ordinary pipettes are emptied at one delivery into the weighing bottle, those of burettes and measuring pipettes in portions of 2-10 c.c. at a time, according to the accuracy desired; the conditions with regard to delivery and the interval allowed for draining as practised at the National Physical Laboratory being observed. If Mohr's system is used, the weight for the normal temperature chosen must be calculated according to the Table on p. 33. For the true litre the data given on p. 21 *et seq.* are to be observed, and Tables I. and II. (pp. 23 and 24) used for the necessary corrections. The error of the vessel is then given by the difference between the calculated additional weight and that actually required.

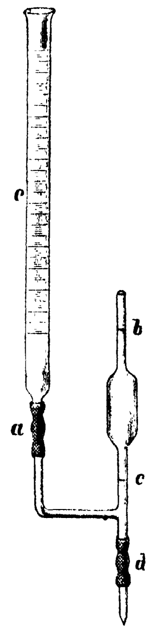


FIG. 12.

At least two calibrations should be made, and more if there are large differences in the determinations, and from the mean of the results a table of corrections is drawn up. In the case of measuring flasks and ordinary pipettes, it is preferable to alter the graduation to the corrected position.

If a great many calibrations have to be carried out the delay due to weighing may be avoided by the use of standard measuring instruments, although this is less accurate than direct weighing. For this purpose the Ostwald pipette (Fig. 12) is usually employed. These pipettes are made to hold 2 or 5 c.c., according to the degree of accuracy required, and are tested as follows. The pipette is fitted on to the lower end of the burette as shown, the burette is filled with water of the normal temperature, and then by opening a pinch-cock at *a* the pipette is filled exactly up to the mark *b*. A weighing bottle is then placed below the pipette, the pinch-cock at *d* opened, and the water allowed to flow out until it just reaches the mark *c*, one or preferably two minutes being allowed to elapse for completion of the delivery. If this interval is allowed, it is unnecessary to connect the side tube

of the pipette with the jet of the burette, instead of, as is shown here, with the rubber tubing. The mean of three weighings of the contents of the pipette, if they agree well among themselves, is taken as the standard. To calibrate the burette *e*, it is filled with water at any desired temperature, which, however, must remain constant during the calibration; then, by opening *a*, the water is allowed to rise to *c*, and the burette filled to the zero mark. By again opening *a*, the water is allowed to rise exactly to *b*, and a reading of the burette taken. The water in the pipette is next allowed to run out to *c* by opening *d*, and the pipette again filled up to the mark *b* by opening *a*; the position in the burette is again read off, and so on until the burette is empty. An interval of a minute is allowed to elapse before each reading in *e*, *b*, or *c*. The mean of two series of experiments is taken, and the actual capacity of each interval of the burette, corresponding to the capacity of the pipette, is thus determined. If, for example, the capacity of the pipette determined by the use of Table I. has been found to be 2·1234 true c.c., and if the first pipette delivery occupies 2·20 c.c. in the burette, each c.c. of the burette $= \frac{2\cdot20}{2\cdot1234} = 1\cdot036$ c.c. If the reading of the burette after the second delivery is 4·35 c.c., each c.c. in this section contains $\frac{4\cdot35 - 2\cdot20}{2\cdot1234} = 1\cdot013$ c.c., and so on. In this way a correction table or curve for the burette readings can be constructed.

Cushman[1] mentions an improvement on the Ostwald pipette which Ostwald himself had previously adopted, which consists in graduating the upper narrow tube, care being taken that the capacity of the pipette from the mark *c* to about the middle of the upper tube *b* is 2 c.c. It is then not necessary to determine the capacity of the pipette by a number of accurate weighings as above, but only to find the value of the pipette scale with regard to the burette scale by a few determinations. In calibrating, 2 c.c. at a time are allowed to pass from the burette into the pipette, and the height of the liquid in the latter noted; the corrections of the burette can thus be calculated. This calibration is of course only relative; if the absolute values of the graduations are required, the capacity of the pipette must be determined in the ordinary way. Or it may be found by making a few weighings, so as to ascertain up to which of the graduations on the upper tube the pipette has to be filled so that it holds exactly 2 c.c.; it is subsequently always filled up to this mark, and used for calibrating according to the method described above, whereby the corrections to be applied to the readings of the burette can be found without much calculation. For calibrations according to the true litre, attention must be paid to the details on p. 21 *et seq.*

[1] *J. Amer. Chem. Soc.*, 1901, **23**, 482; *Chem. News*, 1902, **85**, 77.

The temperature of the volumetric solutions should really be always the same as that at which the burette was calibrated, and this temperature should be indicated on the vessels (*e.g.*, $\frac{15^\circ}{4^\circ}$, $\frac{17^\circ.5}{17^\circ.5}$, etc.) From this point of view some prefer the calibration to be made at 17°·5 or 20°, because these temperatures approximate more to the average laboratory temperature. Small deviations from the normal temperature can be overlooked, as their effect falls within the limits of experimental error, but a considerable error is introduced by working at a temperature of say 8° to 10° or even lower, as often happens in works' laboratories in winter, or, on the other hand, when the temperature rises to 25° or more in summer, as may occur in the best laboratories. Under such circumstances if the temperature differs from the normal by more than 2°, the necessary corrections are imperative. In most cases these corrections may be made with sufficient accuracy on the basis of the expansion of distilled water; if greater accuracy is required, the tables drawn up by A. Schulze [1] for a number of normal solutions may be used. For correcting readings when the temperature of the water exceeds 15°, use may be made of the following table, calculated by Schloesser for the expansion coefficient of glass = 0·000027, and the values for the expansion of water given by the Physico-technical Reichsanstalt. The figures given in the table are the number of c.c. which must be subtracted from 1000 c.c. to give the volume of distilled water which at *t*° fills a litre flask, calibrated at 15°, so that it occupies a volume of 1000 c.c. at 15°.

Temp.	c.c.	Temp.	c.c.
15°	0·000	23°	1·348
16°	0·130	24°	1·563
17°	0·272	25°	1·788
18°	0·42	26°	2·023
19°	0·58	27°	2·267
20°	0·76	28°	2·520
21°	0·94	29°	2·782
22°	1·14	30°	3·053

This table holds for the apparent expansion of distilled water. The values for *N*/5 and *N*/10 solutions differ so slightly from these, that the table may also be used for these solutions. For *N*/1 solutions, on the other hand, the deviations are greater: for hydrochloric acid, the expansion between 15° and 25° may be taken as 2·42 per cent.; for oxalic acid, 2·62 per cent.; for sulphuric acid, 3·05 per cent.; for sodium hydroxide, 3·15 per cent., and for sodium carbonate, 3·03 per cent.

In using such solutions errors may also be introduced by working at temperatures differing appreciably from that at which the solutions were standardised. For instance, in the case of normal hydrochloric

[1] *Z. anal. Chem.*, 1882, 21, 167.

acid, standardised at 15°, readings made at 10° must be divided by 0·9991 and readings at 20° by 1·0011, in order to avoid an error of ± 0·1 per cent.; for normal sulphuric acid the error is about 1½ times greater than for distilled water.

Apparatus for Volumetric Analysis

The ordinary apparatus used in volumetric analysis, such as measuring flasks, measuring cylinders, pipettes and burettes, is familiar to every technical chemist, and is fully described in text-books on analytical chemistry. Attention may, however, be advantageously directed to a few points of importance for technical laboratory work.

Burettes and Pipettes.

The cheapest and most convenient of the various forms of burette is that shown in Fig. 13, in which the exit tube is closed with a glass bead, thus dispensing with a metal pinch-cock.

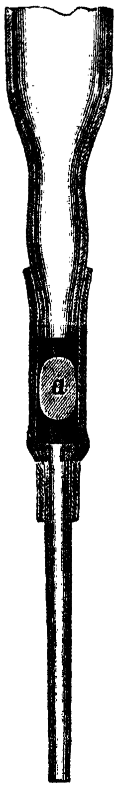


Fig. 13.

By squeezing the rubber tube outside the bead *a*, it takes the form shown in Fig. 13A, thus leaving a space at each side through which the liquid flows out; with a little practice in the manipulation, the liquid can be allowed to escape as quickly or as slowly as may be desired. This arrangement lasts much longer than any of the various forms of pinch-cock, with their accompanying rubber tubes; it is, of course, inapplicable to potassium permanganate and iodine solutions.

Fig. 13A.

When used in the control work of manufacturing processes, no special precautions in reading burettes are necessary. For more accurate laboratory work, however, the following precautions are necessary:—

In order to be fairly certain of reading burettes of 50 c.c. capacity, and graduated in $\frac{1}{10}$ c.c. to within 0·01 c.c., the use of a pocket lens is advantageous; it is also necessary to avoid two sources of uncertainty, namely, the indistinct boundary between air and liquid, and the parallax error. The first is generally avoided by taking the lower boundary line of the black meniscus as the normal reading, but this cannot be done in the case of dark liquids such as permanganate solution. The boundary line is rendered much sharper by shutting off the light from below, by placing a strip of black paper behind the burette, with the upper edge not more than 1 mm. below the meniscus, as recommended by the National Physical Laboratory; the strip can be conveniently held by an ordinary wire paper-clip. The meniscus so shaded should be viewed against a white background.

P. Schellbach[1] recommends the use of burettes with two narrow white longitudinal strips separated by a dark-coloured (blue) strip down the back of the burette; in this way a fine point, which can easily be read, is formed at the boundary of the meniscus.

The second source of uncertainty is due to parallax. If the eye is not quite accurately in the plane of the meniscus, the reading may be several hundredths of a c.c. too high or too low. This is obviated by having a circular mark for reading, which appears as a single line when the eye is exactly in its plane. For this purpose Erdmann devised the cylindrical float, which is, however, open to the objections that it often sticks, especially when the burette is being filled, and that the greater accuracy of reading hoped for from its use is rendered quite illusory by its frequently taking an oblique position and by the unequal capillary rise of the liquid between its exterior wall and the inside wall of the burette. For these reasons most chemists have abandoned its use.

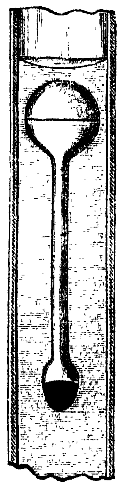


FIG. 14.

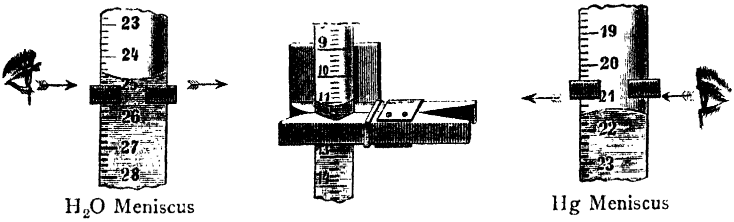
The spherical float of Beutell[2] (Fig. 14), in which capillary effects are obviated, is a considerable improvement on that of Erdmann. With a good float of this kind, which takes a true vertical position, an experienced observer can read quite well to 0·01 c.c. and in any case with much greater certainty than without a float, when ordinary burettes without circular marks are used.[3] These floats are often not properly weighted, and consequently hang obliquely; they are then quite useless.

Ordinary floats cannot be used for fairly strong permanganate solution, on account of its dark colour. The double spherical float proposed by Rey,[4] one sphere of which projects above the liquid and carries the mark, for such solutions, is unsatisfactory, on account of the difficulty of getting floats of this kind which hang vertically and also because the upper sphere is too small. The floats constructed by Diethelm[5] are somewhat better, but the upper bulb is also unavoidably too small.

The problem of avoiding parallax and at the same time attaining a sharper reading is very satisfactorily solved by the use of the light screen constructed by Göckel[6] (Fig. 15), which renders both floats and circular graduations unnecessary. It is a blackened clamp which is placed on the burette 2 to 3 mm. below the lowest point of the meniscus; owing to its diagonal form, it can be fitted to tubes of from 9-20 cm. diameter with one and the same clamp. The black clamp shades off

[1] *Chem. Zeit.*, 1885, **8**, 1515. [2] *Z. angew. Chem.*, 1889, **2**, 8.
[3] *Cf.* G. Lunge, *5th Congress of Applied Chemistry*, 1903.
[4] *Ber.*, 1891, **24**, 2098. [5] *Chem. Zeit.*, 102, **26**, 607.
[6] *Chem. Zeit.*, 1903, **27**, 1036. *Cf.* also G. Lunge, *Z. angew. Chem.*, 1904, **17**, 198.

the superfluous light, thus forming a very sharp, dark boundary line. If necessary, especially when the light is not very good, a sheet of white paper or a small piece of frosted glass may be held behind the burette,



H_2O Meniscus

Hg Meniscus

FIG. 15.

or fixed to the back of the clamp. The new feature in Göckel's screen is the avoidance of parallax, by making the opening of the screen exactly at right angles to its horizontal surfaces. Small metallic plates, screwed to the clamp, act in such a way that on opening and closing the screen its motion is always in the same plane. In order to avoid parallax, therefore, it is only necessary to bring the eye into such a position that the front and back edges of the upper surface of the screen coincide. The same object can be obtained for a mercury meniscus by placing the screen 2 to 3 mm. *above* it, as shown in the figure. The screen can also be employed for avoiding parallax errors in dealing with opaque solutions, such as permanganate, although the meniscus is, of course, not visible.

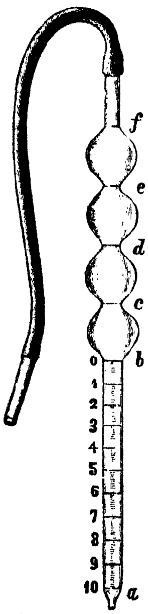


FIG. 16.

In addition to the ordinary pipettes the measuring pipette suggested by O. Bleier,[1] shown in Fig. 16, is useful for technical analysis. It is designed to deliver quantities up to say 50 c.c. by means of one and the same pipette, according as the point *b*, *c*, *d*, *e* or *f* is taken as zero. The capacity from *b* to *c*, *c* to *d*, *d* to *e*, and *e* to *f*, must always be exactly 10 c.c., and the connecting tubes must not be too wide, as otherwise the practical value of the device is lost.

When one and the same volume of liquid has often to be measured off, self-adjusting pipettes (overflow pipettes) are very suitable, especially when large amounts (50 to 100 c.c.) have to be taken. There are many forms of these pipettes, of which those shown in Figs. 17 and 18 are examples.

It must not be overlooked that, even under the most favourable circumstances, measuring in pipettes is far less accurate than weighing. The procedure very generally and advantageously adopted for technical

[1] *Chem. Zeit.*, 1897, **21**, 1028.

work, of weighing out a large amount of substance, dissolving it in a measuring flask and withdrawing an aliquot part of the solution for analysis, is never as accurate an analytical operation as the weighing out and direct analysis of a small amount of substance, even if the measuring vessels have been carefully calibrated. The advantages of the latter method may, however, be more than counterbalanced by the difficulty of obtaining a satisfactory average sample in small bulk.

FIG. 17.

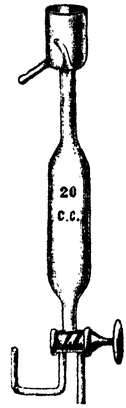


FIG. 18.

Quality of the Glass employed in volumetric analysis.

Attention to the quality of the glass of which the measuring vessels, beakers and flasks, employed in volumetric work, are made, is of importance. It has long been known that many kinds of glass are gradually attacked even by distilled water, and more readily by alkalis, with the liberation of both silicic acid and of alkali. Glass is much more resistant towards acids. Many investigations have been carried out on this subject, which will be dealt with in the section on "*Glass*" in Volume III.

INDICATORS FOR ACIDIMETRY AND ALKALIMETRY[1]

A dissolved substance which changes colour when the acidity (or hydrogen ion concentration) of a solution, in which it is present, is varied, is a possible indicator. The factors on which the practical utility of an indicator depend will be discussed later.

Most of the indicators at present in use are either weak acids or weak bases or amphoteric substances. Thus the pure substances are but slightly ionised in aqueous solution, but on addition of alkali to an acid indicator (or of acid to a basic one) salt formation occurs with greatly increased ionisation. A change in colour is observed owing to the fact that the ions have a different colour to that of the non-ionised substance. Phenolphthalein, for example, is a weak acid, which in dilute solution in water is colourless, and gives a hydrogen ion concentration of the order of 10^{-9} at ordinary temperatures. On addition of alkali, the well-known red colour of the ions of the salt

[1] For details see the following monographs:—*The Theory and Use of Indicators*, E. B. R. Prideaux, 1916; *Die Theorie der Alkalimetrischen und Azidimetrischen Titrierungen*, N. Bjerrum, Ahrens' Sammlung, xxi.; *Der Stand der Indikatoren Frage*, A. Thiel, Ahrens' Sammlung, xvi.; *Indikatoren der Azidimetrie und Alkalimetrie*, F. Glaser, 1901; *The Determination of Hydrogen Ions*, W. Mansfield Clark, 1920; *Der Gebrauch von Farbenindicatoren*, I. M. Kolthoff, 1922.

appears, which can further be changed to colourless again by acidification, with formation of the original weak acid.

The colour change is now considered to be due not merely to the formation of ions, but to more fundamental changes in the structure of the complex molecule of the indicator. The behaviour of indicators which change colour at several points as the hydrogen ion concentration is varied continuously, and the effect of adding alcohol, etc., to the solution, together with many other phenomena, can scarcely be explained by the use of the ionic theory of the action of indicators as stated above. It is therefore supposed that changes of a tautomeric character take place concurrently with the formation of salts.[1]

These theoretical views give rise to important practical considerations when indicators are used in acidimetry and alkalimetry. First, the range of hydrogen ion concentration in which the colour change occurs must correspond to that concentration which obtains at the end point it is wished to observe; secondly, the colour change must not lag behind the variation in hydrion concentration, as happens, for instance, with cyanin and hæmatin, owing to the slowness of the tautomeric transformation; thirdly, the colour change must be independent of factors other than the hydrion variation, and it must be easily visible in ordinary illumination. Other desirable conditions, such as the exact coincidence of a vivid and sharp colour change with the point of neutralisation, are more difficult to achieve in practice.

The more commonly used indicators will now be reviewed from the point of view of their colour changes. It is convenient to record the concentrations between which the colour changes take place (the *range* of the indicator) as the negative logarithm of the hydrion concentration expressed in gram ions per litre (pH). Thus the change of methyl orange from red to yellow begins at a hydrion concentration of $10^{-2.9}$ and is complete at a concentration of $10^{-4.0}$. The range of the indicator is therefore 2·9 to 4·0. Absolute neutrality (*i.e.*, the hydrion content of the purest water) is expressed by the exponent 7·07 at 18°, and E. Salm[2] gives the following table of concentration of hydrochloric acid which have whole number exponents:—

Normality of HCl solution	1·35	0·103	0·0104	0·001
pH	0·0	1·0	2·0	3·0

A 0·001 normal sodium hydroxide solution has a concentration of hydrogen ions of $10^{-12.13}$.

The older classification of indicators as (*a*) insensitive to acids, sensitive to alkalis; (*b*) half sensitive to acids and to alkalis (neutral point); (*c*) sensitive to acids, insensitive to alkalis, corresponds roughly to the ranges, (*a*) 0 to 6, (*b*) 6 to 8, (*c*) 8 to 14 respectively.

[1] For a general discussion see B. M. Margosches, *Z. angew. Chem.*, 1907, **20**, 181.

[2] *Z. Elektrochem.*, 1904, **10**, 341.

Methyl orange.

This indicator is the sodium salt of *p*.dimethylaminoazo-benzene *p*.sulphonic acid, $SO_2ONa.C_6H_4.N:N.C_6H_4.N(CH_3)_2$, and was introduced by Lunge.[1] It is a widely used indicator of class (*a*).

The free acid is red, and if obtainable, is less likely to be adulterated with dextrin, etc. A 0·1 per cent. solution in water is convenient for general use. Its range as mentioned above is from 2·9 to 4·0, the colour changing from red through orange to yellow. The colours are easily visible, except in turbid or very dilute solutions, in artificial light; they are, however, discharged by nascent sulphurous acid and by nitrous acid.

Methyl red.

Methyl red has come into increased use as an indicator during the last few years. It is *p*.dimethylaminoazo-benzene *o*.carboxylic acid, $(CH_3)_2N.C_6H_4.N:N.C_6H_4.COOH$. Its range, according to S. P. L. Sörensen, is 4·2 to 6·3, the colour changing from red to yellow. It is recommended generally by E. Rupp and R. Loose,[2] who state that it can be used for $N/100$ solutions, also by R. T. Thomson[3] and by F. Lehman and G. Wolff[4]; S. A. Kay and S. H. Newlands[5] have used it for determining hardness of water, S. Minovici and C. Kollo[6] for titrating picric acid. It will be seen that its range lies between those of methyl orange and litmus, rather overlapping the latter. The colour change, however, is sharper than that of litmus. It is necessary, as with litmus, to boil the solution when titrating carbonates. A 0·1 per cent. solution of the indicator in water is used.

Litmus.

Litmus is a typical neutral point indicator, still widely used. It is sold in cubes, made up with chalk and gypsum, containing 4 to 5 per cent. of the active colouring matter, and can be purified as follows. The cubes are boiled thrice with 85 per cent. alcohol to remove inert colours, and are then extracted with hot water, the clear liquid decanted and concentrated. The excess of potassium carbonate present is neutralised with acetic acid, and evaporation continued to a syrupy stage. The residue is covered with 90 per cent. alcohol, the solution filtered, and the precipitate dissolved in water to give the litmus solution. This procedure, however, merely adds to the cost of a relatively expensive and not very useful indicator. The solution, also,

[1] *Chem. Ind.*, 1881, 4, 348; *Ber.*, 1878, 11, 1944.
[2] *Ber.*, 1908, 41, 3905.
[3] *Analyst*, 1914, 39, 518.
[4] *Arch. Pharm.*, 1917, 255, 113
[5] *J. Soc. Chem. Ind.*, 1916, 35, 445.
[6] *Bull. Acad. Sci. Roumaine*, 1914-15, 3-61.

does not keep in absence of air, and a trace of phenol is a desirable addition. Litmus has a wide range (5·0 to 8·0) and the change in colour from red to blue is perceptibly gradual, even on addition of strong acids. The colours are not so easily seen in artificial light as in daylight.

Phenolphthalein.

Phenolphthalein is a triphenylmethane derivative, being the anhydride of dihydroxy-triphenyl-carbinol-carboxylic acid, and has the structural formula—

$$\begin{array}{l} \diagup C_6H_4 . OH \\ C—C_6H_4 . OH \\ |\diagdown C_6H_4 . CO . O \\ |\underline{\qquad\qquad\qquad}| \end{array}$$

It was introduced as an indicator by Luck.[1] It is used in 0·1—1·0 per cent. solution in 50 to 90 per cent. alcohol. Its range is 8·3 to 10·0, with an easily visible colour change from colourless (acid) to pink (alkaline). The reverse change is less conspicuous, while excess of concentrated alkali discharges the red colour irreversibly. It is a typical indicator of the third class (*c*), and is most useful in titrating weak acids with strong, carbonate-free alkalis. Recently, the *phenol sulphophthaleins* and *phenol tetrachlorophthaleins* have been suggested as superior substitutes for phenolphthalein by S. F. Acree[2] and co-workers.

For details of the many other indicators which have been suggested and used, reference must be made to the monographs quoted above. G. S. Walpole[3] has summarised the data for some recent indicators. Of these, 2.5-*dinitrohydroquinone* may be mentioned as an indicator with several change points, viz.:

*p*H.	2	4	6	8	10	12
Colour . .	Green yellow	Orange yellow	Orange	Brown red	Red purple	Purple

Mixed Indicators often give more conspicuous or more useful colour changes than single substances. Thus a mixture of *p*-nitrophenol (range 5 to 7) and phenolphthalein changes from colourless to yellow and then to red on addition of alkali. The intermediate colour is a warning that the neutralisation approaches completion. M. E. Scholtz[4] has suggested a number of mixtures of indicators which are useful in practice.

[1] *Z. anal. Chem.*, 1877, **16**, 3202.
[2] *J. Amer. Chem. Soc.*, 1916, **38**, 2772; 1918, **40**, 1940; 1919, **41**, 1031.
[3] *Biochem. J.*, 1914, **8**, 628.
[4] *Z. Elektrochem.*, 1904, **10**, 549.

The Application of Indicators.

The application of indicators to acidimetry and alkalimetry is dependent on the variations in hydrion concentrations round about the neutral point. These changes are best shown by a curve in which – log [hydrion concentration] is plotted against the actual concentrations of acid and alkali. Such neutralisation curves are available for the commoner acids and alkalis, and they can be constructed either by calculation from the usual ionisation formulæ or determined experimentally by measurement of the E.M.F. set up between the acid

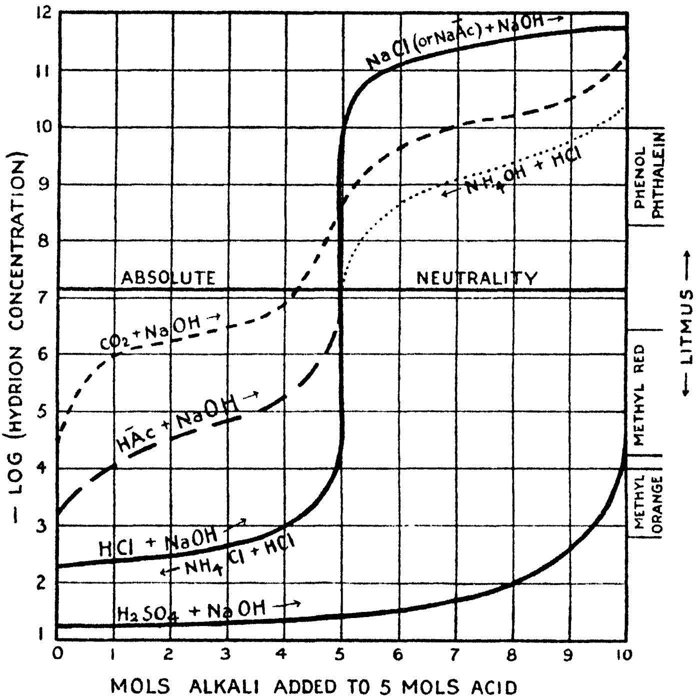


FIG. 19.—Neutralisation curves in 0·005 normal concentration.

solution at a hydrogen electrode and a standard solution and electrode. A few such curves for 0·005 normal solutions are given diagrammatically in Fig. 19.

When a strong monobasic acid, *e.g.* hydrochloric acid, is neutralised by a strong base, the hydrion concentration is but slightly changed until 90 per cent. of the necessary alkali has been added, after which it decreases rapidly, and finally, as the neutral point is approached, passes through many powers of ten on addition of minute quantities of alkali. The reverse change is equally sharp, and it is clear from the curve that any indicator of range lying between 4 and 10 will serve for

the titration. Methyl orange will give a slight error on the acid side, but methyl red, litmus, and phenolphthalein give accurate results provided no carbonate (or other salt of a weak acid) is present in the alkali used.

Weaker acids like acetic acid suffer a reduction in hydrion concentration to 10^{-6} before the neutral point is approached with any rapidity. Hence indicators of ranges below 6 are useless for such titrations (*e.g.*, methyl orange), for the alkaline colour appears before neutralisation is complete. Thus phenolphthalein or other fairly high exponent indicator is used to titrate weak acids, including most common organic acids, with caustic alkalis.

Conversely, when a weak base like ammonia is neutralised by hydrochloric acid, hydrion concentrations as high as 10^{-8} are obtained before the curve bends rapidly towards the vertical neutral portion. Here phenolphthalein is useless and methyl red should be used, for methyl orange is open to the same objection as in the case $HCl-NaOH$, for after neutralisation the curves coincide in the lower half.

Still weaker bases (*e.g.*, aniline) give curves in which, except when acid is first added, the slope is gradual, and there is no vertical neutral portion. The titration of such bases with strong acids requires an indicator of carefully selected and restricted range. Thus aniline has been titrated with hydrochloric acid, using as indicator dimethylaminoazobenzene, which changes from red to flesh colour at 10^{-8} concentration of hydrion. Very weak acids (*e.g.*, phenol) give similar indefinite curves.

A problem which frequently arises is the titration of a base in presence of a weak acid, in other words, the titration of a salt. In such cases the hydrion concentration due to the liberated weak acid is low, so that an indicator of small exponent can be employed. Accordingly, methyl orange is used for titrating carbonates, bicarbonates, silicates, borates, arsenites, and sulphides with strong acids to determine the total alkali therein.

The titration of total acid in the salts of weak bases (such as aniline, toluidine, quinoline, and most alkaloids) can similarly be carried out, using a high exponent indicator like phenolphthalein, for the liberated weak base does not sufficiently reduce the hydrion concentration to affect the indicator.

The neutralisation curves of *polybasic acids* are similar to those of monobasic acids when the acids are strong (compare for example the curves for sulphuric acid and hydrochloric acid in Fig. 19). Hence they can be titrated to complete neutralisation by the use of methyl red, litmus, etc. Citric acid, again, can be titrated as a tribasic acid with caustic alkalis, using phenolphthalein as indicator, as it gives a curve similar to that of acetic acid. When, however, phosphoric acid is

titrated with sodium hydroxide, a sharp variation in hydrion concentration occurs at the stage NaH_2PO_4, which gives a concentration of 10^{-4}. This point can therefore be determined by the use of methyl orange. A second rapid variation occurs at 10^{-9} corresponding to Na_2HPO_4, so that the acid behaves as dibasic when phenolphthalein (range 8·3 to 10·0) is used. The formation of Na_3PO_4 is not indicated by an abrupt change in hydrion concentration, and, as this point is also far on the alkaline side of absolute neutrality, it cannot be accurately found.

Carbonic acid, as can be seen from Fig. 19, gives an end-point at exponent 8·3 corresponding to formation of bicarbonate, so that phenolphthalein can be used to fix this stage in the neutralisation of carbonates with acids. Methyl orange or tropæolin OO give an end-point corresponding to liberation of all the carbon dioxide present.

This end-point, in actual practice, is more acid than shown on the curve, as the presence of sodium chloride increases the acidity of the carbonic acid. The successive use of phenolphthalein and methyl orange in the same solution is employed to estimate mixtures of alkali carbonates with hydroxide or with bicarbonate.

Naturally, if the solution is boiled when carbonates are being titrated, so that the weak carbonic acid is removed, the hydrion concentrations are those of the neutralisation of a base by a strong acid, and consequently litmus or phenolphthalein may be used to determine the end-point. It is desirable, however, to complete the titration in the cold, as changes in temperature affect both the range of the indicator and the ion concentration due to any given acid solution. The errors due to this effect and other ionic considerations have been worked out by Bjerrum.[1]

The effect of neutral salts on the colour changes of indicators is varied, and in cases of doubt the final colour should be matched against a solution of the salts formed (or otherwise present) which has been tinged with the indicator, and just brought to the end-point colour. Congo red (range 3 to 5) is so notably affected by salts that its general usefulness is impaired. Alcohol and other organic liquids produce more profound changes in many indicators, and matching of the final colour is imperative when titrating alcoholic solutions. A well-known application of this effect is in titrating *Boric acid*, when addition of glycerol or mannitol converts the neutralisation curve of this weak acid into one similar to those of strong acids, thus permitting accurate titration with alkali hydroxide and phenolphthalein.

The trouble of preparing comparison solutions on each occasion (for the colours change if the solutions are kept) can be avoided by the use of coloured liquids made from inorganic salts, as recommended by J. W. McBain.[2]

[1] *Loc. cit.*

[2] *J. Chem. Soc.*, 1912, 101, 814.

Turbid or *coloured solutions* can also often be titrated by the method of matching; or monochromatic light, or a pocket spectroscope as recommended by A. Tingle,[1] is useful for observing the colour change of the indicator in these solutions. J. Houben[2] uses a trace of ferrous salt in presence of hydrogen sulphide, which gives a black colour when free alkali is present.

Test Papers.

Test papers are made by immersing previously washed and dried filter paper (or note paper) in a solution of the indicator, coloured by very dilute acid or alkali as may be required. The paper is then dried in a neutral atmosphere, with occasional changes in position to distribute the colour. Such papers are useful for testing gases for acidity or alkalinity, or as a means of using the indicator externally, when for some reason it cannot be added to the solution in the usual way. When only a qualitative test for acidity or alkalinity is required, papers made from indicators of ranges round about seven will obviously be most sensitive. Hence litmus paper is widely used. Lacmoid is used for much the same purposes, but the red paper is more sensitive to alkalis (range 4 to 7). Dichromates are acid, normal chromates alkaline, to lacmoid. Methyl orange paper can be used to detect strong acids in presence of weak, but congo red is preferred for this purpose owing to the more striking colour change from red to dark blue on addition of acids. Turmeric (yellow) turns brown with alkalis (free or as carbonates) or with alkaline earths, but is most used for testing for boric acid and uranium salts.

All test papers must be kept in air-tight receptacles, as the vapours in the air of an ordinary laboratory rapidly render them useless.

Electrometric Titration.

The titration of acid and alkaline liquids consists in the addition of one to the other until a certain concentration of hydrion is attained. Indicators provide one means of finding when the required concentration is reached, but in some cases a direct measurement of the hydrion concentration is desirable.

The usual method is to compare the potential difference at a hydrogen electrode immersed in the solution which is being titrated, with that at a standard (*e.g.*, calomel-potassium chloride) electrode, the two solutions being connected by a tube filled with potassium chloride solution. The neutralisation curves of many acids and bases have been worked out in this way by W. Bottger[3] and J. H. Hildebrand,[4]

[1] *J. Amer. Chem. Soc.*, 1918, **40**, 873.
[2] *Ber.*, 1919, **52** [B], 1613.
[3] *Z. physik. Chem.*, 1897, **24**, 253.
[4] *J. Amer. Chem. Soc.*, 1913, **35**, 847.

who give details of the apparatus. An electrode particularly suited to technical work is described by H. J. S. Sand.[1]

The electrometric method is most commonly employed in cases where indicators cannot be used. In determinations of the acidity or alkalinity of physiological solutions the presence of proteins interferes with the reliability of most indicators. G. S. Walpole[2] has applied the electrometric method for this purpose; and H. J. S. Sand, J. T. Wood, and D. J. Law[3] have used it for determining the acidity of tan liquors, which are too highly coloured to admit of the use of indicators. Other applications have recently been described by J. Pinkhoff,[4] G. A. Freak,[5] H. S. Roberts,[6] W. D. Treadwell and L. Weiss,[7] I. M. Kolthoff,[8] and W. S. Hendrixson,[9] with apparatus adapted to the various purposes.

For the use of measurements of electrical conductivity in analytical operations, see pp. 223-227.

NORMAL SOLUTIONS

A large number of standard solutions are used in technical analysis; those employed only for special purposes are treated of in the sections in which their applications are discussed, the present section being restricted to a description of the standard solutions in general use, and which are employed in various branches of technical work.

General considerations.—A normal solution of a substance may be defined as a solution which contains one gram-equivalent of the substance per litre of solution. Such concentration is shown by the abbreviation N or $N/1$, and, similarly, $N/2$, $N/5$, $N/10$, indicate solutions of $\frac{1}{2}$, $\frac{1}{5}$, and $\frac{1}{10}$ the normal concentration respectively.

The equivalent of an acid is the weight which contains one gram of displaceable hydrogen, so that the equivalents of monobasic acids are the same as their molecular weights in grams (*e.g.*, HCl, 36·47; HNO_3, 63·02). The equivalent of a dibasic acid, such as sulphuric acid, is half the gram-molecular weight; in that case, therefore, 49·04 grams. The equivalents of alkalis may be defined as the weights required to neutralise the equivalent of strong acid. So that the equivalent of sodium hydroxide is one mole, *i.e.*, 40·01; whereas the equivalent of the di-acid base barium hydroxide is half the gram-molecular weight, *i.e.*, 85·69 grams.

From these definitions it is clear that one litre of normal acid will

[1] *J. Soc. Chem. Ind.*, 1911, **30**, 872.

[2] *Biochem. J.*, 1913, **7**, 4, 418.

[3] *J. Soc. Chem. Ind.*, 1911, **30**, 3, 872.

[4] *Pharm. Weekblad*, 1919, **56**, 1218. *Chem. Weekblad*, 1919, **16**, 1163, 1168.

[5] *J. Chem. Soc.*, 1919, **115**, 55.

[6] *J. Amer. Chem. Soc.*, 1919, **41**, 1337, 1358.

[7] *Helv. Chim. Acta*, 1919, **2**, 680.

[8] *Rec. Trav. Chim.*, 1921, **40**, 532.

[9] *J. Amer. Chem. Soc.*, 1921, **43**, 14, 858, 1309.

exactly neutralise a litre of any normal alkali, or, more generally, equal volumes of such solutions will react exactly with each other. This conclusion indicates the great utility of normal (or *N*/2, *N*/5, etc.) solutions, for the same standard acid or alkali can be used for a variety of purposes with the minimum of calculation.

In general, the solution which contains one gram-equivalent of the active portion of a substance per litre is taken as the normal solution. Oxidising agents (for example, potassium permanganate) are made up to contain the equivalent (8 grams) of available oxygen per litre; accordingly a tenth normal solution of this salt will contain 3·161 grams per litre since the gram molecular weight (158·03) yields 40 grams of oxygen for oxidising purposes. Similarly a *N*/10 solution of potassium dichromate contains 4·903 grams per litre, as one mole of the salt (294·2 grams) gives 48 grams available oxygen.

Normal solutions are particularly useful, as indicated above, when a number of different determinations are to be made, using the same standard solution. When, however, it is required to determine frequently the strength of a single commercial product, it is better to make up the standard solution to correspond with a simple weight of the substance to be determined, say 1, 5, or 10 grams per litre. Thus a solution of silver nitrate which is to be used entirely for the determination of sodium chloride should be made up to contain 2·907 grams silver nitrate per litre, so that each c.c. corresponds to 0·001 g. sodium chloride. A normal solution has no advantages in such cases.

Sometimes, again, the quantities required for a standard solution are merely empirical. Thus, in the valuation of tanning materials by Löwenthal's method, it is necessary to standardise the permanganate against an actual tannin under conditions similar to those under which the determinations are to take place.

In only a few cases can the standard solution be made by the simple process of weighing out the requisite quantity of the substance concerned, and after dissolving it, diluting the solution to the required volume. It is usually necessary to make first an approximate solution and then to standardise it by means of substances of known purity.

Standard Acids

With the exception of oxalic acid and a few other acids, it is not possible to take even an approximately exact weight of anhydrous acid for the purpose of making a standard solution. It is therefore necessary to dilute the pure concentrated acids to approximately the required strength, a final adjustment of the volume being made after standardisation. The normality of ordinary concentrated acids is shown in the

following table, together with the volume required to make a litre of approximately normal solution :—

Acid.	Sp. Gr.	Normality.	c.c. to be diluted to 1000.
Acetic Acid	1·058	17·3 *N.*	57·5
Hydrochloric Acid . .	1·16	10·0 *N.*	100·0
Nitric Acid	1·42	16·0 *N.*	63·5
Sulphuric Acid . . .	1·854	37·0 *N.*	27·0

Of these acids, hydrochloric acid is the most useful in volumetric analysis. It is preferable to sulphuric acid owing to its wider applicability, as, for example, in titration of the alkaline earths. It has a greater avidity in the cold, and being monobasic, no complications arise from hydrolysis of acid salts. Its concentration, also, can be accurately controlled gravimetrically by precipitation with silver nitrate.

Hydrochloric acid can also be used in place of nitric acid, except for the estimation of chlorides in an alkaline solution (for example, crude caustic soda) with silver nitrate, using potassium chromate as indicator; in this case an amount of standard nitric acid just sufficient to neutralise the alkali is added, this amount having been found from a previous titration with hydrochloric acid. For this purpose, however, a standardised nitric acid is not really necessary, for, if an excess of acid has been added, it can be neutralised by a slight excess of sodium hydroxide or sodium carbonate, without disturbing the subsequent titration with silver nitrate.

Many different substances have been suggested as a *basis or standard for acidimetry and alkalimetry*, of which the following are the most important.

Sodium carbonate takes precedence of all the others, both on account of its extensive use and of its actual merit. It can be prepared and weighed out absolutely pure and free from water with the greatest ease, and can be very accurately titrated with hydrochloric acid and methyl orange, and, with proper precautions, with litmus or with phenolphthalein. "Chemically pure sodium carbonate," free from any appreciable amount of chloride, can be obtained commercially; it can also be readily prepared from sodium bicarbonate which has been freed from chloride and sulphate, if present, by washing with small amounts of cold distilled water. The sodium carbonate must be quite free from sodium oxide as well as from water.

If pure commercial sodium carbonate is used as a standard, it must dissolve in water to a perfectly clear solution, give no turbidity with silver nitrate after neutralisation with nitric acid, and no reaction for

sulphates, after excess of hydrochloric acid has been added. In applying these tests a sufficient amount must be dissolved, say 2 to 3 g., and the solution sufficiently diluted, in order to avoid precipitation of barium chloride. A very slight opalescence with silver nitrate is often noticed, but it is easy to judge if an amount of chloride sufficient for quantitative estimation is present. If the sodium carbonate is pure, it is dried by heating in a platinum crucible, preferably in a sand bath to 270° to 300°, with continual stirring, until the weight is constant; half an hour is sufficient for this purpose, exclusive of the time required to attain the temperature. The sand is packed round the outside of the crucible to the same height as the sodium carbonate inside, and a thermometer is placed quite close to, or even in, the crucible. This method is quite as convenient as heating with the naked flame.

Sodium bicarbonate can be obtained commercially of a sufficient degree of purity for the preparation of the carbonate; it should be tested, as above, for the presence of insoluble impurities, chlorides, and sulphates, of which the two latter can be removed by washing, owing to the slight solubility of the bicarbonate. The second equivalent of carbon dioxide and the water can then be driven off by heating in a platinum crucible, as described for sodium carbonate. Lunge[1] has shown that the bicarbonate is completely converted into the carbonate by heating, for a few minutes, at 260° to 270°; if heated for from a half to one hour in a sand bath or in an air bath at a temperature not over 300°, the carbonate can be relied on as being free from bicarbonate, water, and sodium oxide.

Although sufficiently pure bicarbonate can readily be obtained commercially, yet it may at times be necessary to purify an impure product, so as to obtain a pure substance for standardising purposes. Reinitzer[2] gives the following method of purification. About 250 c.c. of distilled water is heated to 80° in a tall beaker (preferably of Jena glass) and the bicarbonate added, in small quantities at a time, till the solution is saturated, the liquid being continually stirred; during this process, part of the carbon dioxide is evolved, with effervescence. When nothing further dissolves, the solution is filtered through a pleated filter paper, preferably in a hot-water funnel, into a flask and cooled to 10°. The crystals which separate are filtered by suction in a funnel fitted with a platinum cone only, and are washed several times with small quantities of cold water, which is completely removed by suction after each addition. The salt is then dried thoroughly, ground, and mixed, and the small quantities to be employed in standardising are heated as required in a sand bath to a temperature not exceeding 300°, as above.

The possibility of preparing sodium carbonate quite free from

[1] *Z. angew. Chem.*, 1897, 10, 522. [2] *Ibid.*, 1894, 7, 551.

moisture and from sodium hydroxide has, from time to time, been questioned by various investigators.[1] Lunge[2] has, however, shown that the product obtained by the method of ignition given above is quite free from moisture, and that the quantity of sodium hydroxide formed is negligible for all ordinary analytical work; in a special experiment to test this point, he found only 0·004 per cent. of the hydroxide in a sample of carbonate dried at 270° to 300°.

For standardising or controlling the strength of a normal acid, the corresponding quantities of sodium carbonate must always be weighed out separately; the plan of preparing a normal sodium carbonate solution containing say 53 g. to the litre and withdrawing aliquot portions for the different estimations, is unsatisfactory. Errors in measuring, in the emptying of pipettes, etc., cannot be avoided, even when standardised apparatus is employed, and the inaccuracy arising from these causes is much greater than errors of weighing.

Sörensen[3] has recommended the use of *sodium oxalate* as the basis for alkalimetry instead of sodium carbonate; it has the advantage of being applicable also as a standard for oxidation methods of volumetric analysis. The salt can readily be obtained free from water of crystallisation, and is not hygroscopic. As prepared according to his directions, by Kahlbaum, by precipitation with alcohol and drying at 240°, it may be employed for standardising purposes, either directly or after a few hours' heating in the steam oven. An accurately weighed quantity of the salt is carefully heated, for a quarter to half an hour, in a covered platinum crucible, over a small gas flame, supported in a hole in an asbestos card, so as to avoid contamination by sulphur compounds from combustion, or over a spirit lamp,[4] until the sodium carbonate formed just begins to fuse; towards the end of the operation the lid is moved aside so as to cover about one-half of the crucible, to promote the complete combustion of the carbon formed. A mixture of sodium carbonate, containing a little sodium hydroxide, is thus formed, which is not weighed, but transferred along with the crucible to a tall beaker, moistened with water, treated with an excess of the acid to be standardised and warmed on the water bath; the solution is then poured into a conical flask, the crucible and cover and the beaker rinsed out, ten drops of a solution of phenolphthalein added and boiled till the carbon dioxide is completely expelled, in a current of air freed from carbon dioxide, cooled in cold water, and the excess

[1] *Cf.* C. L. Higgins, *J. Soc. Chem. Ind.*, 1900, **19**, 958; Sörensen and Andersen, *Z. anal. Chem.*, 1905, **44**, 156; B. North and W. Blakey, *J. Soc. Chem. Ind.*, 1905, **24**, 396; Sebelien, *Chem. Zeit.*, 1905, **29**, 638.

[2] *Z. angew. Chem.*, 1904, **17**, 231; 1905, **18**, 1520.

[3] *Z. anal. Chem.*, 1897, **36**, 639; 1903, **42**, 333; 1905, **44**, 156.

[4] *Cf.* Lunge, *Z. angew. Chem.*, 1905, **18**, 1520.

of acid titrated back with $N/10$ sodium hydroxide. The equivalent of sodium oxalate is $\frac{134 \cdot 01}{2} = 67 \cdot 005$, so that 10 c.c. of an $N/10$ acid correspond to 0·067005 g. of sodium oxalate; or 0·1 g. of the salt = 14·92 c.c. of an $N/10$ acid. In a subsequent paper,[1] Sörensen gives accurate directions for the examination of commercial "pure" sodium oxalate, for impurities.

Sörensen's investigations were carried out with great care, and they show that very good results are obtainable with sodium oxalate, as a basis for alkalimetry; but the examination of the substance as regards absolute purity is more troublesome and tedious than in the case of sodium carbonate, and this is true of the whole process, even if the titration is not carried out with phenolphthalein in boiling solution as above, which is quite unnecessary, but with methyl orange in the cold.[2] There is, therefore, no reason for giving sodium oxalate the preference over sodium carbonate, but it can be advantageously used as a control in doubtful cases.

To prepare an $N/1$ hydrochloric acid solution, pure hydrochloric acid is diluted as shown in the table given above (p. 47), or to a specific gravity of about 1·020, so as to obtain a preliminary acid somewhat over the normal strength (36·47 g. HCl per litre). This acid is then titrated against a freshly ignited sample (2 – 2·5 g.) of sodium carbonate. Since w grams of carbonate require $\frac{w}{0 \cdot 053}$ c.c. of a normal solution, the actual volume of the prepared acid, say x c.c., will be smaller than this; the acid must therefore be diluted by taking $\frac{53 \cdot 0\,x}{w}$ c.c. and diluting to a litre.

The diluted acid is then titrated against new samples of freshly ignited sodium carbonate as a check. A further control, by determining the proportion of chlorine by silver nitrate, is also very desirable; 10 c.c. of the acid (= 0·3647 g. HCl) should give 1·4334 g. AgCl.

All normal solutions should be prepared at 15°, and a correction must be applied as detailed on p. 33, if they are subsequently employed at a temperature differing by more than 1° or 2° from 15°.

Of other substances which have been suggested for the standardising of normal acids and alkalis, the following are the most important.[3]

Grandeau,[4] and subsequently Pincus[5] and Fresenius,[6] suggested the

[1] *Z. anal. Chem.*, 1903, **42**, 512. [2] *Cf.* Lunge, *Z. angew. Chem.*, 1905, **18**, 1520.

[3] Many of the following references are taken from a paper by Vanino and Seitter, *Z. anal. Chem.*, 1902, **41**, 141, which contains a fairly complete summary of the literature on volumetric solutions and substances used in standardising them. *Cf.* also B. North and W. Blakey, *J. Soc. Chem. Ind.*, 1905, **24**, 396.

[4] *Z. anal. Chem.*, 1863, **2**, 426. [5] *Ibid.*, 1863, **2**, 426.

[6] *Quantitative Analysis*, 7th edition, vol. ii., p. 194.

use of *calcspar* (Iceland spar), which they regard as chemically pure calcium carbonate, but this is not always the case. Thiele and Richter [1] found deviations of 0·2 per cent. from the true value, with this substance.

Hartley [2] and Neitzel [3] have made use of metallic *sodium*.

Borax is recommended by Salzer,[4] Rimbach and Worms,[5] Richmond,[6] Buchanan,[7] and Perman and John.[8]

Ammonium chloride has been suggested by Reinitzer,[9] and by Seyda and Weinig,[10] and *ammonium sulphate* by Knublauch.[11]

An *iodometric method*, based on the reaction :—

$$5KI + KIO_3 + 6HCl = 6I + 3H_2O + 6KCl,$$

is described by Mohr, Kjehdahl,[12] Gröger,[13] and Fessel.[14] v. Than [15] proposed *potassium bi-iodate*, which is also recommended by Meineke.[16] Riegler [17] has suggested pure *iodic acid*. All the iodometric methods for preparing normal acids and alkalis are indirect, and the sum of the small unavoidable errors may easily exceed the permissible limit. The basis of iodimetry is not more certain than that of acidimetry, if pure sodium carbonate is used as the standard, but rather the contrary, so that acidimetry may justifiably be employed as a basis for iodimetry rather than the reverse.

The iodometric method is recommended by Petersen [18] for determining the amount of acid in coloured plant extracts, roots, beer, etc.

Morse and Chambers [19] base a method of standardisation on the decomposition of neutral *hydrogen peroxide* by potassium permanganate. Another method, involving measurement of a gas, in which potassium iodide, potassium iodate, sodium hydroxide, and hydrogen peroxide are employed, has been proposed by A. Baumann.[20]

Hart and Croasdale [21] and Kohn [22] have proposed the electrolysis of *copper sulphate* as a basis for acidimetry. The advantage of this proposal lies in the fact that it is dependent only upon the ratio of copper to sulphuric acid. Dauvé [23] states that good results cannot be obtained by this method, because if no free acid is present, the deposited copper does not adhere to the electrode and contains suboxide of copper, but no experiments are given to support this

[1] *Z. angew. Chem.*, 1900, **13**, 486.
[2] *Z. anal. Chem.*, 1873, **12**, 89.
[3] *Ibid.*, 1893, **32**, 122.
[4] *Ibid.*, 1893, **32**, 449.
[5] *Ibid.*, 1896, **35**, 338 ; 1897, **36**, 688.
[6] *Chem. News*, 1895, **72**, 5.
[7] *J. Soc. Chem. Ind.*, 1904, **23**, 1093.
[8] *Chem. News*, 1895, **71**, 296.
[9] *Z. anal. Chem.*, 1895, **34**, 577 ; 1900, **39**, 458.
[10] *Z. angew. Chem.*, 1892, **5**, 204.
[11] *Z. anal. Chem.*, 1882, **21**, 165.
[12] *Ibid.*, 1883, **22**, 327.
[13] *Z. angew. Chem.*, 1890, **3**, 353 and 385.
[14] *Z. anorg. Chem.*, 1899, **23**, 67 ; 1904, **38**, 449.
[15] *Annalen*, 1891, **261**, 358.
[16] *Chem. Zeit.*, 1895, **19**, 2.
[17] *Z. anal. Chem.*, 1896, **35**, 308 ; 1899, **38**, 250.
[18] *Ibid.*, 1903, **42**, 308.
[19] *Ibid.*, 1898, **37**, 183.
[20] *Ibid.*, 1892, **31**, 450.
[21] *J. anal. Chem.*, 1890, **4**, 424 ; 1892, **6**, 421.
[22] *J. Soc. Chem. Ind.*, 1900, **19**, 962.
[23] *J. Pharm. Chem.*, 1902, **16** [2], 65.

conclusion. Meade[1] has described the preparation of standard sulphuric acid, and indirectly of standard hydrochloric and nitric acids, by the electrolysis of copper sulphate.

North and Blakey[2] recommend sodium bicarbonate for fixing the strength of standard acids, but according to Lunge[3] it is not reliable.

Normal hydrochloric acid can of course be prepared and checked gravimetrically, by precipitation with silver nitrate. Lunge finds that with careful working, the results by this method agree with those obtained by the use of sodium carbonate to within 0·05 per cent., sometimes even to within 0·02 per cent.; he does not regard this gravimetric method as more accurate than standardisation with pure sodium carbonate.

It is much more difficult to attain the same degree of accuracy with normal sulphuric acid by precipitation with barium chloride, owing to the well-known difficulty of obtaining absolutely pure barium sulphate.

Several authors have recommended evaporating down the acids with ammonia, and weighing the ammonium salt formed.

Moody[4] has suggested the preparation of normal hydrochloric acid, by passing hydrochloric acid gas into a known weight of water, and determining the increase in weight. The method has since been studied and improved by Higgins[5]; very accurate results can be obtained, but somewhat special apparatus is required which is hardly suitable for technical work. Both Roth[6] and Raschig[7] have also described this method. The constant boiling mixture of hydrogen chloride and water originally suggested by Roscoe and Dittmar[8] has been recommended by Hulett and Bonner[9] as a basis for preparing normal solutions.

A. Marshall[10] recommends the preparation of normal sulphuric acid on the basis of its specific gravity. This proposal has been extended to hydrochloric acid by Küster and Siedler,[11] but the examples given show too great deviations from the actual strength, even in cases regarded by them as correct up to 0·5 per cent., to allow of the recommendation of the method, for accurate work. In a later communication,[12] Küster and Münch state that the method is correct to within ±0·0001 of the sp. gr. Tables of specific gravities of sulphuric acid and of hydrochloric acid, between the limits of $N/10$ and $N/1$ solutions,

[1] *J. Amer. Chem. Soc.*, 1901, **23**, 12 and 343.
[2] *J. Soc. Chem. Ind.*, 1905, **24**, 396.
[3] *Z. angew. Chem.*, 1905, **18**, 1520.
[4] *J. Chem. Soc.*, 1897, **73**, 658.
[5] *J. Soc. Chem. Ind.*, 1900, **19**, 958.
[6] *Z. angew. Chem.*, 1904, **17**, 710; *J. Soc. Chem. Ind.*, 1904, **23**, 837.
[7] *Z. angew. Chem.*, 1904, **17**, 577.
[8] *J. Chem. Soc.*, 1860, **13**, 128.
[9] *J. Amer. Chem. Soc.*, 1910, **31**, 390.
[10] *J. Soc. Chem. Ind.*, 1900, **19**, 4; 1902, **21**, 1511.
[11] *Chem. Zeit.*, 1902, **26**, 1055; *Ber.*, 1905, **38**, 150.
[12] *Ber.*, 1905, **38**, 150; *Z. anorg. Chem.*, 1905, **43**, 373.

have also been prepared by Worden and Motion;[1] such tables may very well be used for the approximate adjustment of volumetric solutions.

Quincke[2] has proposed a method, depending upon the measurement of oxygen evolved from potassium ferrocyanide and alkaline hydrogen peroxide.

There are several methods, in which an acid substance is taken as the basis, by means of which an alkaline solution is standardised and the latter then employed for standardising a normal acid.

The most important of the compounds used in this way is *oxalic acid*, the value of which, as a basis for acidimetry, has been advocated by Mohr. It is, however, very difficult to prepare oxalic acid quite pure, and with the definite proportion of water corresponding to the formula $H_2C_2O_4.2H_2O$. This difficulty is by no means overcome by Hampe's suggestion[3] to use the extremely hygroscopic anhydrous acid, which sublimes at 100°, instead of crystallised oxalic acid. Of the numerous methods proposed for the preparation of pure oxalic acid, that of C. Winkler is most largely used.[4] 500 g. of commercial oxalic acid are dissolved in an equal weight of boiling hydrochloric acid of sp. gr. 1·07, in a porcelain basin, the solution placed in ice water and allowed to crystallise, with continual stirring; the finely crystalline mass is transferred to a funnel, provided with a plug of glass wool, allowed to drain, and washed several times with hydrochloric acid. It is then redissolved in pure boiling hydrochloric acid, again cooled with continual stirring, the crystals filtered off, washed with a little water and recrystallised by dissolving in just the requisite amount of boiling water. The finely crystalline mass thus obtained is again washed and the whole treatment is repeated two or three times. The final product is left to dry in a cool place, the drying material being repeatedly changed. Thus prepared, it is free from chlorine and mineral matter, but still contains enclosed liquid, and must therefore be dehydrated before use. This is best effected by drying for five to six hours at 60°, as oxalic acid volatilises to a considerable extent at 100°. The dry acid having the formula $H_2C_2O_4$, must naturally be kept in tightly closed bottles; when it is to be employed for standardising purposes, about 0·2 g. is weighed out into each of several weighing tubes, again dried for several hours at 60° to 80°, allowed to cool in the closed tubes, and then accurately weighed.

To carry out the method, a normal alkali is first standardised with the oxalic acid and then used for adjusting the strength of the normal acid; the method is, therefore, indirect, and accordingly liable to small unavoidable errors which do not arise in direct standardisation.

[1] *J. Soc. Chem. Ind.*, 1905, **24**, 178.

[2] *Z. anal. Chem.*, 1892, **31**, 1.

[3] *Chem. Zeit.*, 1883, **7**, 73 and 106.

[4] *Uebungen in der Massanalyse*, 3rd edition, p. 69.

G. Bruhns[1] states that the most accurate method of using oxalic acid as a basis for alkalimetry is to titrate its solution with alkali until it is nearly neutralised, then to add sufficient calcium chloride to precipitate the whole of the oxalic acid and to complete the titration after the addition of methyl orange.

Potassium tetroxalate is regarded by many as a more reliable basis for alkalimetry. The crystallised salt has the formula $KHC_2O_4.H_2C_2O_4.2H_2O$; its employment was first suggested by Kraut,[2] and subsequently recommended by Ulbricht and Meissl,[3] and by Meineke,[4] whilst Wells,[5] Hinmann,[6] and Dupré and Kupffer[7] have criticised its value adversely. The tetroxalate has been again strongly recommended by J. Wagner,[8] who frees it from moisture by pressing between blotting paper, instead of by standing over sulphuric acid, as recommended by Meineke, and employs it in the air-dried state. The tetroxalate is used for standardising barium hydroxide with phenolphthalein as indicator, and the strength of the normal acid adjusted from the hydroxide.[9] The same method is recommended by Kühling.[10] Lunge[11] states that, as the result of a large number of experiments, he has not succeeded in obtaining potassium tetroxalate with a constant proportion of water corresponding to the formula given above. F. W. Babington and A. Tingle[12] have used *tartaric* and *salicylic acids* as basic substances for standardising barium hydroxide with good results.

Objection must be made on principle to standardisation with oxalic acid, potassium tetroxalate and all other substances, such as potassium bi-iodate and cream of tartar, with which phenolphthalein is used as indicator, when the normal solutions are subsequently used with methyl orange.

Potassium bi-iodate has been recommended as a basis for the direct adjustment of normal sodium carbonate by Meineke[13] and by E. Crato,[14] and *potassium hydrogen tartrate* has been recommended as a standard by Bornträger.[15]

Normal oxalic acid is still used by some chemists, and is required for a few purposes, such as the examination of Weldon mud. It cannot be employed with methyl orange as indicator, and even for the estima-

[1] *J. prakt. Chem.*, 1916 (ii.), **93**, 73, 312; *J. Soc. Chem. Ind.*, 1916, **35**, 908; 1917, **36**, 545.
[2] *Annalen*, 1863, **126**, 629.
[3] *Z. anal. Chem.*, 1887, **26**, 350.
[4] *Chem. Zeit.*, 1895, **19**, 2.
[5] *Ibid.*, 1894, **33**, 456.
[6] *Z. anal. Chem.*, 1893, **32**, 453.
[7] *Z. angew. Chem.*, 1902, **15**, 352.
[8] *Proc. 5th International Congress for Applied Chemistry*, 1903.
[9] J. Wagner, private communication.
[10] *Z. angew. Chem.*, 1903, **16**, 1030; *Chem. Zeit.*, 1904, **28**, 596 and 612.
[11] *Z. angew. Chem.*, 1904, **17**, 227; *Chem. Zeit.*, 1904, **28**, 701.
[12] *J. Soc. Chem. Ind.*, 1917, **36**, 1203.
[13] *Chem. Zeit.*, 1895, **19**, 2.
[14] *Massanalytische Tafel.*
[15] *Chem. Zeit.*, 1881, **5**, 519; *Z. anal. Chem.*, 1886, **25**, 333; 1892, **31**, 56; 1894, **33**, 713.

tion of the hydroxides of the alkaline earths, in the presence of their carbonates, it can be completely replaced by hydrochloric acid.[1]

It is prepared by dissolving 63·03 g. of chemically pure crystallised oxalic acid in one litre for the normal acid, and correspondingly smaller amounts for the weaker acids; since the preparation of absolutely pure and dry oxalic acid, according to the method detailed on p. 53, is so troublesome, normal oxalic acid for use should be prepared of approximate strength from the ordinary "pure" acid, and the strength determined by titration with accurate normal alkali.

The more concentrated solutions, including the $N/1$ acid, are fairly stable; if sterilised, they can be kept in the dark for some years without alteration in strength. Very dilute solutions such as the $N/100$ acid, used in water analysis for the determination of "organic matter," keep only for a very short time, and must be prepared fresh on each occasion. The strength can, of course, readily be determined, at any time, by titration with sodium hydroxide, using litmus or phenolphthalein as indicator; in order to obtain accurate results, the solution should be boiled with a slight excess of sodium hydroxide, cooled quickly, and titrated back in the cold, in order to avoid error owing to the presence of sodium carbonate in the hydroxide.

The Strength of Normal Acids.

In works, $N/1$ acid is used for controlling working processes and for many laboratory purposes; the change of colour of the indicator with acid of this strength is very sharp under all circumstances. Its use necessitates taking a correspondingly larger amount of substance for analysis, and in practice, a sufficient degree of accuracy is attainable, with less carefully calibrated weights and measuring vessels than are used for other work. It is, however, often necessary to work more accurately, and there is then the choice of $\frac{1}{2}$, $\frac{1}{5}$, or $\frac{1}{10}$ N acid. These are most readily prepared by dilution of the normal acid; the strength of the diluted acid must always be checked as directed on p. 50, for which purpose 1·000 to 1·250 g. of sodium carbonate is weighed out for the $N/2$ acid, 0·4 to 0·5 g. for the $N/5$ acid, and 0·2 to 0·25 g. for the $N/10$ acid. It is undesirable to have too many normal solutions in use, and usually one other acid besides the normal acid suffices; $N/5$ acid is the best strength for the dilute acid. Very little is gained by using $N/2$ acid, instead of the normal, and $N/10$ acid is too dilute to use as the weaker solution; at least two drops of it are required to bring about a sharp change of colour, so that it is really not more accurate than $N/5$ acid, only one drop of which is required to effect the same result. Titrations to within one drop of an $N/5$ solution (0·02 to 0·03 c.c.) are as

[1] Küster, *Z. anorg. Chem.*, 1898, **18**, 127; Lunge, *Z. angew. Chem.*, 1897, **10**, 41.

near as can be relied upon, taking into account the lack of sensitiveness of many indicators and other sources of inaccuracy.

In works, a large quantity of normal acid is usually prepared at once, say 50 to 60 litres, the capacity of an acid carboy. For laboratory use it must, of course, be transferred to smaller vessels, such as stoppered bottles, holding at most 5 litres; this is preferably done as soon as the acid has been standardised. If, however, the carboy has to be emptied gradually, care must be taken to stopper it well, and to shake thoroughly before use. The smaller bottles must also be well shaken once a day before use, since water may evaporate and condense in the upper empty part of the vessel.

The equivalent of 1 c.c. of $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{5}$, and $\frac{1}{10}$ N acids, in grams of the substance to be estimated, is given in the following table:—

	$N/1$	$N/2$	$N/5$	$N/10$
Potassium Hydroxide	0·05611	0·02805	0·01122	0·005611
Potassium Oxide	0·04710	0·02355	0·00942	0·004710
Potassium Carbonate	0·06910	0·03455	0·01382	0·006910
Sodium Hydroxide	0·04001	0·020005	0·008002	0·004001
Sodium Oxide	0·03100	0·01550	0·00620	0·003100
Sodium Carbonate	0·05300	0·02650	0·01060	0·005300
Barium Hydroxide	0·08569	0·04284	0·01714	0·008569
Barium Carbonate	0·09868	0·04934	0·01974	0·009868
Strontium Hydroxide	0·06082	0·03041	0·01216	0·006082
Strontium Carbonate	0·07382	0·03691	0·01476	0·007382
Calcium Hydroxide	0·03704	0·01852	0·007408	0·003704
Calcium Oxide	0·02804	0·01402	0·005608	0·002804
Calcium Carbonate	0·05004	0·02502	0·010008	0·005004
Magnesium Oxide	0·02016	0·01008	0·004032	0·002016
Magnesium Carbonate	0·04216	0·02108	0·008432	0·004216

Standard Alkalis

The hydroxides of sodium, potassium, ammonium, and barium are employed as standard alkalis; of these, the first is most largely used. The only reason for using the more expensive potassium hydroxide is that it has rather less action on glass.

Ammonium hydroxide has been recommended as a standard alkali because it does not readily absorb carbon dioxide from the air and has no action on glass. These advantages, the first of which is only relative, are, however, counterbalanced by the tendency of the solutions to give up ammonia. Even $N/2$ and $N/5$ solutions alter in strength so rapidly that they cannot be used for any length of time without control; such solutions should not be allowed to stand, even for a short time, in burettes which are not thoroughly shut off from the air.

Barium hydroxide, which absorbs carbon dioxide from the air, giving a precipitate of the carbonate, can only be used when all the

usual precautions are taken to obviate this source of error. It is difficult to prepare a normal solution and still more difficult to keep its strength unaltered, so that a correction factor has always to be used. It is only in certain cases that the advantages of barium hydroxide are sufficient to counterbalance these drawbacks, as, for example, in the titration of weak acids with phenolphthalein, since, unlike the hydroxides of potassium and sodium, it can readily be obtained free from carbon dioxide. When this is of no advantage, as in all cases in which methyl orange is used as indicator, nothing is gained by its use.

Küster and Grüters[1] recommend that barium hydroxide should always be used for accurate determinations with phenolphthalein, because potassium and sodium hydroxides give uncertain results, owing to the variable amounts of contained carbonate.

Sodium hydroxide.—In technical laboratories and even for most scientific purposes, the commercial white caustic soda may be used directly for preparing this solution, since the impurities usually present, such as chloride, sulphate, silicate, and aluminate, very seldom affect the result. Sodium hydroxide in sticks, purified by alcohol, answers all requirements. The expensive product prepared from metallic sodium contains not only sodium carbonate, but sometimes gives a flocculent residue on solution. A similar residue is often obtained when ordinary caustic soda is used, and a sample should therefore be selected which dissolves in water to a clear solution; otherwise the solution must be allowed to settle and the clear liquid decanted.

To prepare normal sodium hydroxide, clear transparent lumps of the best white commercial caustic soda are picked out, any opaque parts on the surface scraped off, and 50 g. weighed out for each litre. It is then dissolved in water, made up to the litre at 15°, and 50 c.c. of this provisional solution titrated with accurately normal hydrochloric acid, using methyl orange as indicator. If n c.c. of acid are used, the number of c.c. of the preliminary alkali, which must be diluted to a litre with pure water to obtain accurately normal sodium hydroxide, is $\frac{50 \times 1000}{n}$.

The solution must, of course, be titrated again to check its accuracy. More dilute solutions are similarly prepared.

Bousfield and Lowry[2] have shown that standard solutions of sodium hydroxide can be prepared from metallic sodium. Küster[3] has also described a method for the preparation of pure sodium hydroxide solutions from the metal.

It is not advisable to prepare very large amounts of sodium

[1] *Z. anorg. Chem.*, 1903, **35**, 459.
[2] *Phil. Trans.*, 1905, **204**, 253.
[3] *Z. anorg. Chem.*, 1904, **41**, 472. *J. Soc. Chem. Ind.*, 1904, **23**, 1027; 1906, **25**, 982.

hydroxide at once as a stock solution, because it slowly attacks the glass and alters a little in strength. In order to obtain accurate results when litmus or phenolphthalein are used as indicators, the hydroxide must be prepared free from carbon dioxide, and when in use, especially in the burette, must be carefully guarded from contact with this gas.

There is, further, no object in preparing an alkali hydroxide solution free from carbon dioxide, unless its re-absorption from the air is carefully guarded against, when in use. To effect this, the solutions should always be prepared and diluted with boiled, carbon dioxide-free water, the titration should be made, as far as possible, without access of air, and the burette and supply-vessel should be guarded against the absorption of the gas.

Glaser[1] and others contend that the errors due to the small quantities of carbonate contained in solutions of the alkali hydroxides and to the carbon dioxide absorbed from the air during titration, are practically negligible when litmus or phenolphthalein are used as indicators, and may be disregarded. Experiments by Lunge[2] and by Raschig,[3] however, show definitely that this is not the case.

For comparatively rough work, complete protection against the absorption of carbon dioxide is unnecessary when litmus or phenolphthalein are used as indicators; if methyl orange is used, such protection is not required, even for accurate work. With the latter indicator sodium hydroxide cannot advantageously be replaced by a solution of sodium carbonate (53·05 g. in a litre of water at 15° for an $N/1$ solution); for a solution of sodium carbonate also gradually attacks glass, even when cold, taking up a small amount of alkali, and further, the solution creeps up and evaporates at burette jets and on the neck of flasks, thus giving rise to serious errors, unless this action is continuously watched.

Potassium hydroxide solution is made up similarly to sodium hydroxide, allowance being made for its higher molecular weight and also for the greater proportion of impurities that are generally contained, in weighing out the quantity required for the preliminary solution.

Barium hydroxide solution is usually made of empirical strength, as the commercial product always contains barium carbonate. To prepare the solution about 20 g. of the crystallised hydroxide ($Ba(OH)_2 + 8H_2O$) is dissolved in a litre of water, and about 1 g. of barium chloride added in order to remove any alkali hydroxide that may be present. The slightly turbid solution is allowed to settle, and then syphoned into a bottle through which a current of air free from carbon dioxide

[1] *Indikatoren der Acidimetrie und Alkalimetrie*, p. 28.

[2] *Proc. 5th Congress Applied Chemistry*, 1903.

[3] *Z. angew. Chem.*, 1903, 16, 820.

has been previously passed, and which is fitted with a syphon tube and with a guard tube containing soda lime.

In the following table the analytical value of $\frac{1}{1}$, $\frac{1}{2}$, $\frac{1}{5}$, and $\frac{1}{10}$ normal solutions of alkali are given, expressed in grams per c.c. of solution:—

	N/1	N/2	N/5	N/10
Hydrochloric Acid	0·03647	0·018235	0·007294	0·003647
Nitric Acid	0·06302	0·03151	0·012604	0·006302
Sulphuric Acid	0·04904	0·02452	0·009808	0·004904
Phosphoric Acid [1]				
(a) With Methyl Orange	0·07104	0·03552	0·014208	0·007104
(b) „ Phenolphthalein	0·03552	0·01776	0·007104	0·003552
Oxalic Acid [2]	0·06303	0·031515	0·012606	0·006303
Citric Acid [2]	0·07001	0·035005	0·014002	0·007001
Acetic Acid [2]	0·06004	0·03002	0·012008	0·006004

1 The values given are calculated for the anhydride P_2O_5.

2 Towards litmus and phenolphthalein; the values given are calculated for the crystallised acids, including the water of crystallisation for oxalic and citric acids.

Potassium Permanganate

A solution of potassium permanganate is used for oxidising purposes, in which it gives up five-eighths of its oxygen, according to the equation:—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O + 3H_2O.$$

Referring to the explanation given on p. 45, it will be seen that a normal solution would yield 0·008 g. available oxygen per c.c., and would be obtained by making up 31·61 g. pure potassium permanganate to a litre. A solution of this strength would, however, be liable to crystallise at low temperatures, owing to the slight solubility of the salt; hence solutions stronger than *N*/2 are never prepared, and much more dilute solutions are very frequently used, *e.g.*, *N*/10, *N*/20, *N*/50, or even *N*/100. The use of such dilute solutions is consistent with accuracy, since an indicator, in the ordinary sense of the term, is not used; for in the permanganate solution, the very intense colour of the MnO'_4 ion is independent of the corresponding positive ion $H^{\cdot}$ or $K^{\cdot}$, etc. The liquid will, of course, remain colourless as long as the MnO'_4 ion is destroyed and converted into other colourless ions, according to the above reaction; at most, the solution will assume a slight coloration, owing to the formation of ions from other substances taking part in the reaction, *e.g.*, the formation of tervalent from bivalent iron. In the dilute solutions used for these titrations such colorations are extremely slight, and disappear altogether when compared with the colour of the permanganate ion. An excess of even one drop of *N*/100 permanganate solution in 100 c.c. or more water, produces the intense

purple, or in small quantities, light-red colour of the permanganate ion, and thus indicates the end of the reaction.

The main reason for using the standard solution fairly strong is, that otherwise an inconveniently large volume of the solution would usually be required to complete the titration. Another reason why very dilute permanganate solutions should only be used in exceptional cases, is that permanganate acts on the impurities which are present even in ordinary distilled water, and its available oxygen is thus decreased. A freshly prepared permanganate solution should therefore never be used immediately, but should be left to stand for eight to ten days, before it is standardised; the impurities in the water will then be completely oxidised. No appreciable error is incurred if a permanganate solution is diluted with ordinary distilled water and used *immediately*, but dilute permanganate solutions should not be kept in stock; strong solutions (at least 1/10 normal) should be prepared and accurately standardised and diluted to $N/20$, $N/50$, or $N/100$ for immediate use, according to requirements.

Oddy and Cohen [1] state that permanganate solutions lose 2 to 3 per cent. of their oxidising value in four months, whether exposed to light or not. Their observations, however, are insufficient in number and in accuracy. Treadwell [2] found that a well-protected permanganate solution lost only 0·17 per cent. of its oxidising value, after keeping for eight months; he recommends that the solution be re-standardised every two or three months, if great accuracy is required. Lunge has observed a decrease of 0·2 per cent. after three months, and agrees with Treadwell's recommendation.

Permanganate titrations are generally carried out in sulphuric acid solution. Hydrochloric acid has the great disadvantage of acting on potassium permanganate, even in very dilute solution, chlorine being liberated; hence solutions containing chlorides cannot be titrated without special precautions. This point was investigated by Kessler, and subsequently by Zimmermann, who showed that perfect accuracy is attained, provided a fairly large quantity of manganous sulphate is added to the liquid to be titrated; a solution containing 200 g. of the crystallised salt per litre is used, and about 20 c.c. of this solution are added.[3] This has since been confirmed by J. A. N. Friend,[4] G. C. Jones and J. H. Jeffery,[5] and others.

Pure dilute nitric acid is, like sulphuric acid, indifferent to permanganate; the lower oxides of nitrogen, however, reduce permanganate, and this action affords the best method for their estimation.

[1] *J. Soc. Chem. Ind.*, 1890, 9, 17. [2] *Analytical Chemistry*, 5th edition, 1919, vol. ii., p. 603.
[3] For an explanation of this action, *cf.* J. Wagner, *Massanalytische Studien*, p. 77; Gooch and Peters, *Z. anorg. Chem.*, 1899, 21, 185; Skrabal, *Z. anal. Chem.*, 1903, 42, 359.
[4] *J. Chem. Soc.*, 1909, 95, 1228. [5] *Analyst*, 1909, 34, 306.

A normal permanganate solution cannot be prepared by simply dissolving a weighed quantity of potassium permanganate and diluting to a definite volume, partly on account of the above-mentioned action on distilled water, and partly because the "chemically pure" commercial salt generally contains a little potassium sulphate, chloride, nitrate, or other impurities; it cannot be regarded as 100 per cent. potassium permanganate, although Gardner, North, and Taylor[1] have asserted the contrary. For these reasons, a little more than the calculated amount of the salt is weighed out (about 16 g. for $N/2$ solution, 3·2 g. for $N/10$ solution, etc.); this is made up to 1 litre of solution at 15°, and left to stand for about a week before standardisation. It is not advisable to dissolve the salt in the litre flask, as the presence of undissolved crystals may easily be overlooked, owing to the dark colour of the solution. The weighed quantity of the salt is preferably dissolved in warm water in a beaker, the solution poured into the litre flask, and any of the salt that may have remained behind in the beaker then dissolved in more water.

Very many methods have been suggested for fixing the strength of a permanganate solution; only a limited number of these can be referred to, and only a few will be described in detail.

Sörensen has shown, however, that sodium oxalate can be obtained quite pure and free from hygroscopic water, and his recommendation of this salt for the standardisation of permanganate solutions has been fully confirmed by Lunge (cf. *infra*).

1. Sodium Oxalate method.—The use of sodium oxalate was first recommended by Sörensen[2] (*cf.* p. 49). It has no water of crystallisation, is not hygroscopic, and as it can be obtained in a very pure condition is especially suited for the standardisation of permanganate solutions. For accurate work the salt must be placed for a few hours in a drying oven at 100° and left to cool in a desiccator, over calcium chloride. It is then weighed, dissolved in water in a flask, and titrated in sulphuric acid solution at 40°-50°. Ten c.c. $N/10$ potassium permanganate solution correspond to 67·05 mg. sodium oxalate, or 0·1 g. of the latter to 14·91 c.c. of the former. Lunge[3] and M'Bride[4] have confirmed the accuracy of this method, and recommend it, in preference to all others, for the standardisation of permanganate.

Of other oxalates that have been proposed, Kraut[5] has recommended *potassium tetroxalate* (p. 54), Rust,[6] *manganese oxalate*, prepared by precipitation and dried between filter paper, and Barbieri and Neppi,[7] *ferrous oxalate*.

[1] *J. Soc. Chem. Ind.*, 1903, **22**, 731.
[2] *Z. anal. Chem.*, 1903, **42**, 352, 512; 1906, **45**, 272.
[3] *Z. angew. Chem.*, 1904, **17**, 230 and 269; 1905, **18**, 1520.
[4] *Bull. U.S. Bureau of Standards*, 1913, **8**, 611.
[5] *Annalen*, 1863, **126**, 629.
[6] *Z. anal. Chem.*, 1902, **41**, 606; *J. Soc. Chem. Ind.*, 1902, **21**, 1413.
[7] *Rend. Soc. Chim. Roma*, **3**, 16.

2. Oxalic Acid method.—This method, proposed by Hempel, is based on the oxidation of oxalic acid, in presence of sulphuric acid, to carbon dioxide and water:—

$$5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

The reaction proceeds slowly in the cold, rapidly at 40° to 50°; even at this temperature the first drops of permanganate are not immediately decolorised. When once the reaction has started, however, it proceeds rapidly, owing to catalytic action of the manganese salt; the drops of permanganate are then decolorised the instant they reach the liquid, and the final colour change, from colourless to light red, is sudden and very sharp.

The above equation shows that $5 \times 90{\cdot}03 = 450{\cdot}15$ parts anhydrous oxalic acid require 80 parts oxygen; hence one part anhydrous oxalic acid corresponds to 0·17772 parts oxygen. This refers to anhydrous oxalic acid, whilst normal solutions of oxalic acid are prepared from the crystallised acid $C_2H_2O_4 . 2H_2O$, molecular weight 126·06, equivalent 63·03. As Riegler[1] has pointed out, standard oxalic acid solutions may be rendered more permanent by an addition of sulphuric acid and by protecting them from light; nevertheless, these precautions by no means ensure absolute permanence of the solution.

If it be, nevertheless, desired to use this direct method, results of any practical value can only be obtained by using perfectly anhydrous oxalic acid, purified by the somewhat tedious method described above (p. 53). But even when the method is thus modified, it is impossible to be certain that the results will be absolutely reliable. On the other hand, Lunge[2] has shown that accurate results are obtained by preparing a solution from pure, ash-free oxalic acid and determining its strength by first standardising $N/5$ hydrochloric acid with sodium carbonate, the acid being then used to correct a $N/5$ barium hydroxide solution which in turn is used to titrate the approximate oxalic acid solution.

The permanganate, thus standardised, should be used at once to determine the value of a stock of iron wire by method No. 3 described below. When it is subsequently required to standardise permanganate it is more convenient to titrate against this iron wire than against oxalic acid, since the permanence of the latter cannot be relied upon.

3. Iron method.—Very fine soft iron wire is used as the basis of this method; it should be cleaned with emery paper and rubbed with writing paper before weighing. It is, of course, not pure iron and may contain 0·3 per cent. or more of impurity. As Treadwell has pointed out, this does not imply that the value of the wire is equal to that of the contained iron; on the contrary, it may exceed 100 per cent., owing to its

[1] *Z. anal. Chem.*, 1896, **35**, 522; *J. Chem. Soc. Abstr.*, 1896, **70**, 676.
[2] *Z. angew. Chem.*, 1904, **17**, 268.

content of carbon, silicon, phosphorus, etc. To avoid errors, which may be considerable, its value must be determined as described below.

To check an $N/2$ permanganate solution, a piece of wire weighing about 1·25 g., for an $N/10$ solution a piece weighing about 0·25 g., is weighed to within 0·0001 g. The wire is then stretched out, its length measured, and a number of pieces of the same length cut off; these can then be very rapidly weighed, as their approximate weight is known. Each piece will require nearly, but not more than, 50 c.c. of permanganate solution.

The weighed wire is then dissolved in hot dilute sulphuric acid, in absence of air; this may be effected in a flask fitted with a Bunsen valve or in any similar form of apparatus; or a flask provided with a tube, bent twice at right-angles and dipping into a beaker containing sodium bicarbonate solution, may be used. If the flame is removed when the iron has dissolved, the bicarbonate solution is sucked back and cools the contents of the flask, whilst the carbon dioxide evolved keeps out the air.[1] The device (Fig. 20), designed by Contat[2] and improved by Göckel,[3] is much more convenient than any of the above arrangements. It consists of a bulb provided with a syphon overflow tube, which is fitted into the flask in which the iron is dissolved. The amount of water or sodium bicarbonate solution, placed in the bulb

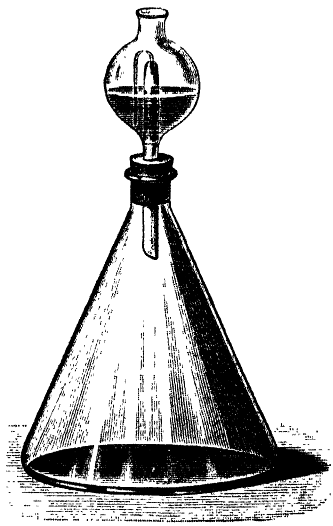


FIG. 20.

at the beginning of the experiment, should be such that the end of the longer arm of the syphon just dips below its surface, and this level is not altered until boiling is finished; a saturated sodium bicarbonate solution is then poured into the bulb, which will be sucked into the flask as the contents cool, until the pressure of the carbon dioxide balances that of the air; the solution remaining in the bulb protects the contents of the flask from the air.

The standardisation of permanganate by means of iron has been subjected to detailed investigation by Skrabal.[4] He found that the apparent value of a sample of iron wire, when determined by permanganate, was 100·03 to 100·21 per cent., whereas the actual amount of iron contained was only 99·38 per cent. (together with 0·03 P,

[1] Jahoda, *Z. angew. Chem.*, 1889, **12**, 87. [2] *Chem. Zeit.*, 1898, **22**, 298.
[3] *Z. angew. Chem.*, 1899, **12**, 620; *J. Soc. Chem. Ind.*, 1899, **18**, 708.
[4] *Z. anal. Chem.*, 1903, **42**, 359.

0·31 Mn, 0·185 Cu, 0·023 S, 0·09 C). He therefore rejects the method as unreliable, and uses either chemically pure iron, or iron wire of known composition, *i.e.*, of definite value; the iron is dissolved in sulphuric acid, 15 c.c. $N/10$ permanganate added to the warm solution, which is then left to stand over-night in a warm place, whereby the carbides are completely oxidised; concentrated hydrochloric acid is then added, the solution heated to boiling, reduced with zinc, and titrated with permanganate. These directions are doubtless good, but uniform and correct results can be obtained without this complication, provided due care is taken to adhere to the same conditions of dilution, heating, etc., both in standardising and in the subsequent use of permanganate.

The cold iron solution is titrated with permanganate until a faint rose-red coloration is obtained, and remains permanent for thirty seconds; it is not necessary that it should be permanent for longer. If the number of c.c. used is divided into the number which would have been required had the permanganate been accurately normal, a coefficient is obtained by which every reading must be multiplied; it is preferable, however, to dilute the solution to the normal value.

In order to avoid the uncertainty due to the composition of the iron wire, Classen has proposed the use of electrolytically deposited iron. The iron is deposited on a platinum dish, by electrolysing a solution of ferrous ammonium sulphate containing ammonium oxalate; the deposited iron is washed with water and alcohol, dried at 80° to 100°, weighed, dissolved in sulphuric acid, and the solution titrated with permanganate whilst still in the dish.

Treadwell[1] also recommends the electrolytic method, which he modifies by depositing the iron on a small cylinder of platinum foil and dissolving it in air-free sulphuric acid, in a current of carbon dioxide.

Skrabal[2] found 0·10 to 1·47 per cent. impurities, including hydrogen, in electrolytic iron obtained by Classen's method. He gives an alternative method for preparing pure electrolytic iron, but according to Classen,[3] the iron thus obtained is not pure.

Avery and Dales[4] have shown that iron, deposited electrolytically from ammonium oxalate solutions, contains 0·21 to 0·42 per cent. of carbon, and that a small quantity of iron, on an average 0·35 per cent., is always left in solution. Whilst Verwer and Groll[5] contend that the deposition is complete and free from carbon, the results of Avery and Dales have been fully confirmed by Kohn, Brislee, and Froysell.[6]

Ledebur[7] states that he has never found the value of iron wire to

[1] *Analytical Chemistry*, 5th edition, 1919, vol. ii., p. 93.
[2] *Z. anal. Chem.*, 1903, **42**, 359.
[3] *Ibid.*, 1903, **42**, 516.
[4] *Ber.*, 1899, **32**, 64 and 2233.
[5] *Ber.*, 1899, **32**, 806; *Chem. Zeit.*, 1901, **25**, 792.
[6] *British Association Reports*, 1900, p. 174.
[7] *Stahl und Eisen*, 1902, **22**, 1242; *cf.* also, Thiele and Deckert, *Z. angew. Chem.*, 1901, **14**, 1233.

exceed 100 per cent., and that it is safe to use the percentage of pure iron present as a basis.

According to Lunge,[1] electrolytic iron cannot be relied upon as pure; on the contrary, its use may lead to errors of several units in the first place of decimals. It is very much better to determine the value of a large stock of iron wire by means of permanganate, after having previously standardised the latter by oxalic acid, referred to pure sodium carbonate (p. 50). Since sodium oxalate is free from all the uncertainties connected with the use of iron, it forms a far more reliable basis for standardisation than the latter.

4. **Ferrous Ammonium Sulphate method.** — The double salt $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$, sometimes called Mohr's salt, is more stable than ferrous sulphate, and was therefore recommended by Mohr for standardising permanganate. The dissolving of the iron is avoided and the errors arising from the variable amount of carbon in iron wire are eliminated. Still greater uncertainty is, however, introduced, owing to the presence of water of crystallisation and of impurities in the salt. Where errors of some tenths per cent. are not of consequence, this salt may be used for standardising; it cannot be recommended for accurate work. The value of the salt is 14·24 per cent. of that of iron, *i.e.*, almost exactly one-seventh.

Meineke[2] also considers ferrous ammonium sulphate to be quite unreliable, and recommends the use of iron alum; this is reduced with stannous chloride, mercuric chloride finally added, and the solution then titrated with permanganate, following Reinhardt's directions.[3] The amount of iron in the "chemically pure" iron alum must be checked by precipitation with ammonia. Brandt[4] has proposed a method in which he prepares "chemically pure ferric oxide"; this is reduced with stannous chloride, and the resulting ferrous solution used to standardise permanganate. Gintl[5] uses a spiral of palladium wire, saturated with hydrogen, as reducing agent, and prefers this to all other methods of reduction.

5. **Volhard's[6] Iodimetric method.**—If a permanganate solution is added to a solution of potassium iodide, acidified with hydrochloric or sulphuric acid, a quantity of iodine is liberated, which is equivalent to the available oxygen in the permanganate. The iodine dissolves in the excess of potassium iodide solution, and its amount can be determined by adding excess of sodium thiosulphate and titrating back with standard iodine solution:—

$$KMnO_4 + 5KI + 8HCl = 5I + 6KCl + MnCl_2 + 4H_2O.$$

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[1] *Z. angew. Chem.*, 1904, **17**, 265.

[2] *Z. öffentl. Chem.*, 1898, **4**, No. 13.

[3] *Stahl und Eisen*, 1884, **4**, 704; *Chem. Zeit.*, 1889, **13**, 323.

[4] *Chem. Zeit.*, 1916, **40**, 605, 630.

[5] *Z. angew. Chem.*, 1902, **15**, 431.

[6] *Annalen*, 1879, **198**, 333; 1887, **242**, 98.

This process, though theoretically quite correct, has the disadvantage of requiring two additional standard solutions, on the accuracy of which the process is dependent; the unavoidable summation of small errors may easily lead to a final error of several tenths per cent. F. Dupré[1] states that the method gives accurate results.

6. Gas-volumetric, Hydrogen Peroxide, or Nitrometer method.[2]—This method, which is of interest as it dispenses with the use of any substance of doubtful purity, is based on the following reaction between hydrogen peroxide and a solution of potassium permanganate, strongly acidified with sulphuric acid:—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Thus, whichever of the reagents is not in excess gives up the whole of its available oxygen, and this is increased by an exactly equal volume of oxygen derived from the other reagent. It is then only necessary to measure the volume of oxygen evolved, to reduce this volume to 0° and 760 mm., and halve the result. The reaction proceeds quite smoothly and is quantitative; the solutions retain no oxygen, since they were previously saturated with air. Certain simple precautions must be observed: viz., a large excess of sulphuric acid must be present, but not too large an excess of hydrogen peroxide; the apparatus must be adjusted immediately the solutions have been mixed, and attention must be paid to those conditions which must be observed in all gasometric methods, such as uniformity of temperature, etc. The latter is easily attained, since the reaction involves no appreciable rise of temperature. Lunge's nitrometer with attached bottle (p. 82) is particularly suitable for the decomposition, and by employing it or similar apparatus, in conjunction with a "gas-volumeter," the calculation of the volume of oxygen to standard conditions is saved.

Since 1 litre of dry oxygen at 0° and 760 mm. weighs 1·429 g. in these latitudes, and half of the evolved oxygen comes from the permanganate, every c.c. of the measured volume corresponds to 0·7145 mg. available oxygen in the permanganate. Hence 1 c.c. of an accurately semi-normal permanganate solution will give 5·597 c.c. of oxygen (N.T.P.); an $N/10$ solution will give 1·119 c.c. oxygen per c.c. of solution, and so on.

The valuation is conducted as follows: 20 c.c. of permanganate solution are accurately measured into the outer compartment of the decomposition bottle and 30 c.c. dilute sulphuric acid (1 : 5) added. For $N/2$ permanganate, 15 c.c. ordinary commercial hydrogen peroxide are then introduced into the inner vessel of the decomposition

[1] *Z. angew. Chem.*, 1904, **17**, 815.

[2] Lunge, *J. Soc. Chem. Ind.*, 1890, **9**, 21. *Cf.* also, H. v. Jüptner, *Osterr. Zeit. für Berg. und Hüttenwesen*, **44**, 371; Vannino, *Z. angew. Chem.*, 1890, **3**, 80; *J. Soc. Chem. Ind.*, 1890, **9**, 552.

bottle, by means of a pipette; for weaker solutions less peroxide is taken. A preliminary experiment should be made, in a beaker, to ensure the presence of an excess of hydrogen peroxide. The decomposition is then carried out in the usual manner (*cf.* p. 82), the volume of evolved gas read after the adjustment of the pressure tube, calculated to N.T.P., allowance of course being made for the tension of aqueous vapour; or the correction may be made by the gas volumeter.

The applications of permanganate are extremely numerous, and include the estimation of iron, oxalic acid and oxalates, nitrous acid and nitrites in sulphuric acid solution, potassium ferrocyanide, tanning materials, and hydrogen peroxide; it is also used indirectly, for titrating back excess of reducing agents, *e.g.*, ferrous oxide in the estimation of nitric acid, nitrates, chlorates, manganese dioxide, peroxides, bleach, etc.

IODIMETRY

The iodimetric methods of volumetric analysis were introduced by Bunsen, and are now very extensively used; they are amongst the most accurate known, owing to the extreme sensitiveness of the indicator, starch solution, that is employed.

Iodine oxidises many substances indirectly, by combining with the hydrogen of water, liberating the oxygen, which then combines with other compounds present. In other cases it combines directly with the hydrogen or sodium in the substance to be estimated, as in the determination of hydrogen sulphide and of sodium thiosulphate.

The "re-sublimed iodine" of commerce is a very pure product, which may be used for many purposes without further purification; for the preparation of normal solutions it only requires to be dried in the exsiccator to free it from water. For accurate standardisation, however, the iodine must be further purified (p. 69).

An $N/10$ iodine solution is generally used; it is prepared as follows: 12·7 g., or a little more, pure re-sublimed iodine are weighed out on a rough balance and shaken into a litre flask containing a solution of 15 to 18 g. potassium iodide in about 30 g. water; the flask is closed, shaken till the iodine is completely dissolved, and then filled up to the mark.

Iodine solutions should be kept in well-stoppered bottles and stored in a cool place; the strength should be checked about once a month, as the contained iodine is distinctly volatile. For this reason the solution, when in use, should be kept out of contact with the air as much as possible, and the titrations should be conducted in bottles or narrow-necked flasks, not in beakers or dishes; for the same reason, the iodine should be run into the solution to be titrated, whenever possible, and not *vice versa.* This does not apply to the titration of

sulphites, since the action of atmospheric oxygen on the sulphite must be avoided (cf. *infra*). The volatility of iodine must also be borne in mind when gases containing sulphur dioxide or sulphuretted hydrogen are bubbled through iodine solution, in order to absorb these gases.

In conjunction with the iodine solution, starch solution is used as the indicator, and either sodium thiosulphate or arsenious oxide solutions, of corresponding strength, as the reducing solution.

Starch solution may be prepared as follows:—3 g. potato starch are ground with a little water to a uniform paste, and gradually added to 300 g. boiling water in a porcelain dish; boiling is continued until an almost clear solution is obtained. This is allowed to settle in a deep vessel, and the clear liquid filtered and saturated with common salt. The solution keeps for a considerable time if kept in a cool place; the addition of mercuric iodide [1] preserves the solution.

Zulkowsky's soluble starch is a more convenient reagent; it is obtained in the form of a thick paste, which should not be allowed to dry up; a small quantity is taken out, on the end of a glass rod, as required for use. Junk [2] sterilises starch solution by boiling with mercury.

Iodine solution is generally standardised by an accurate solution of sodium thiosulphate or of arsenious oxide, the strength of which has been fixed by pure iodine (p. 69).

Kalmann [3] recommends sodium sulphite for the standardisation of iodine. A solution of arbitrary strength is run into the iodine solution until it is just decolorised, when the following reaction takes place:—

$$Na_2SO_3 + 2I + H_2O = 2HI + Na_2SO_4.$$

Thus the acid liberated is exactly equivalent to the iodine. The acid is then estimated by standard potassium hydroxide, using methyl orange as indicator. The method is independent of the amount of water and of sulphate in the sodium sulphite, provided the latter is perfectly free from bisulphite, thiosulphate, and carbonate, a condition difficult to obtain in practice. The decomposition goes best when the solution is not too dilute. One c.c. $N/10$ alkali hydroxide corresponds to 0·012692 g. iodine.

S. W. Young [4] recommends anhydrous sodium thiosulphate for standardising iodine solutions; tartar emetic has been proposed by Metzl,[5] and potassium bichromate by Bruhns [6] and others, and arsenious oxide by R. M. Chapin.[7]

[1] Mutniansky, *Z. anal. Chem.*, 1897, **36**, 220.
[2] *Chem. Zeit.*, 1919, **43**, 258.
[3] *Ber.*, 1887, **20**, 568.
[4] *J. Amer. Chem. Soc.*, 1904, **6**, 1028.
[5] *Z. anorg. Chem.*, 1906, **48**, 156.
[6] *Ibid.*, 1906, **49**, 277; *J. prakt. Chem.*, 1916 [2], **93**, 95, 312; 1917 [2], **95**, 37.
[7] *J. Amer. Chem. Soc.*, 1919, **41**, 351.

The applications of iodine solution, known as iodimetry, generally in conjunction with a corresponding sodium thiosulphate or arsenious acid solution, are very numerous, and include the estimation of sulphurous acid and sulphites; free chlorine and bromine, hypochlorous acid and hypochlorites (including bleach); sulphuretted hydrogen and sulphides; arsenious oxide, peroxides, chloric and chromic acids.

SODIUM THIOSULPHATE

An $N/10$ solution is prepared by dissolving 24·82 g. of the pure crystallised salt $Na_2S_2O_3 . 5H_2O$ in water, which has been completely freed from air by boiling; the solution is diluted to 1 litre with cold air-free water.

Meineke[1] states that pure sodium thiosulphate can be obtained by repeatedly recrystallising the "chemically pure" commercial salt from water, rubbing it to a fine powder with strong alcohol, washing with ether and air drying; but the water content of the thiosulphate prepared in this way is variable.

Pure sodium thiosulphate should dissolve in water without the least turbidity, should give no precipitate with barium chloride (a precipitate would indicate the presence of sulphate, sulphite, or carbonate), and should not redden phenolphthalein (presence of carbonate). It should also be free from sulphide and chloride.

Iodine and sodium thiosulphate react with the formation of sodium tetrathionate, the iodine combining with half the sodium :—

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

Whenever possible, the iodine is added to the thiosulphate solution; the latter should be neutral or faintly acid, because if more strongly acid free thiosulphuric acid is formed, which decomposes on standing into water, sulphur dioxide, and free sulphur. A slight yellow coloration is observed as soon as an excess of iodine is present. The change is sharper in presence of starch solution, but the blue coloration is only obtained at ordinary temperatures. Starch solution must never be added whilst a large excess of iodine is present; the starch should be added towards the end of the reaction, when only very little iodine is present, if the titration is done in this way.

The following method may be used to standardise the thiosulphate solution, and, indirectly, an approximate iodine solution. A small quantity of pure, dry iodine is prepared, by powdering together 0·5 g. pure iodine and 0·1 g. potassium iodide and heating the powder in a small porcelain dish on a sand-bath, or on an asbestos card, until vapour is copiously evolved; the dish is then covered with a dry watch-glass, and the greater part, but not the whole of the iodine,

[1] *Chem. Zeit.*, 1894, **18**, 33.

is sublimed on to the latter. The watch-glass is then covered with a second, accurately fitting glass and the whole weighed, the weight of the two watch-glasses of course being known. The watch-glasses are placed gently in a solution of 1 g. potassium iodide in 10 g. water; after waiting for a moment, to allow the iodine to dissolve, the solution is diluted with 100 c.c. of water and titrated with the thiosulphate solution. (The potassium iodide must be free from potassium iodate; a test for its purity in this respect consists in adding hydrochloric acid to a not too concentrated solution of the salt, when no immediate yellow coloration develops in absence of iodate.) When the colour has been reduced to a pale yellow, a little starch solution is added and the titration continued until the blue colour just disappears. If the thiosulphate solution is of right strength, the amount used in c.c. multiplied by 0·012692 equals the weight of iodine taken.

The following modification of this method recommended by Treadwell[1] is easier to carry out. Two to 2·5 g. pure potassium iodide and not more than 0·5 c.c. water are placed in each of two or three small weighing tubes with tightly fitting, ground stoppers; the tubes are closed and weighed, and then 0·4 to 0·5 g. pure iodine added to each, and weighed again. The iodine dissolves almost instantly in the concentrated potassium iodide solution. One of the tubes is then placed in the neck of a 500 c.c. Erlenmeyer flask, held in an inclined position and containing 200 c.c. of water and about 1 g. potassium iodide. The tube is dropped carefully to the bottom of the flask, the stopper being removed just as it begins to fall, and allowed to follow it. In this way no iodine can be lost. The examples given by Treadwell show deviations of about 0·2 per cent. from each other; these deviations can be reduced to 0·1 per cent., when using the first method given above, after considerable practice.

Winkler has proposed a method for preparing pure iodine in quantity, which consists in adding 5 per cent. potassium iodide and 10 per cent. quicklime (to retain water) to the crude iodine; the mixture is sublimed from a vessel covered with a flask filled with water, on which the sublimed iodine condenses. A funnel, the tube of which is loosely plugged, serves equally well to collect the iodine.

De Koninck's[2] method of preparing pure iodine for standardisation is as follows:—Potassium iodide is freed from potassium cyanide by recrystallising in presence of a little hydriodic acid; one part of the recrystallised salt is then intimately mixed with $1\frac{3}{4}$ parts previously fused potassium bichromate, both having been finely powdered and dried, and the mixture distilled from a small retort, the neck of which fits tightly into a small Erlenmeyer flask.

[1] *Analytical Chemistry*, 5th edition, 1919, vol. ii., p. 646.

[2] *Chem. Zeit.*, 1903, **27**, 192.

Lean and Whatmough[1] consider that the purest iodine is obtained by heating cuprous iodide.

When iodine is kept in a desiccator, the latter should contain calcium chloride and not sulphuric acid, and the cover should not be greased; neglect of these precautions leads to contamination of the iodine, since sulphuric acid is likely to be taken up by the iodine and grease is attacked by iodine vapours, forming hydriodic acid.

Meineke[2] recommends the use of potassium bi-iodate, which had been previously suggested by C. v. Than[3]; the commercial form of this salt is said to be extremely pure and to be quite permanent, even in dilute solution. In acid solution the following reaction takes place:—

$$KH(IO_3)_2 + 10KI + 11HCl = 12I + 11KCl + 6H_2O.$$

Hence 389·95 parts of pure potassium bi-iodate correspond to 1523·04 parts iodine.

This method appears very convenient, particularly for checking thiosulphate solutions, from time to time, by means of a solution of the bi-iodate, but the purity of any commercial bi-iodate cannot be relied upon, as the salt may contain either too much or too little iodic acid. Treadwell[4] also states that commercial bi-iodate cannot be relied upon for direct standardisation. Hence, if it be desired to use potassium bi-iodate, its value must first be determined; this negatives the value of bi-iodate for direct standardisations.

Riegler[5] has recommended crystallised iodic acid for standardising thiosulphate, but Walker[6] has pointed out objections to the method. Kratschmer[7] has suggested sodium bromate, Zulkowsky,[8] and subsequently Crismer,[9] normal potassium chromate, but Meineke[10] has indicated the disadvantages of this last reagent. J. Wagner[11] considers the use of potassium bichromate, under perfectly definite conditions, preferable to other reagents. Dietz and Margosches[12] use potassium chlorate, which, on addition of hydrochloric acid, potassium bromide, and potassium iodide, liberates an exactly equivalent amount of iodine.

N/100 thiosulphate is occasionally required, especially when using *N*/100 iodine; the former must always be freshly prepared, as it does not keep long. Neither is *N*/10 thiosulphate permanent under all conditions. Carbon dioxide acts upon it, in presence of oxygen and sunlight, forming sulphurous acid and free sulphur, and fungoid growths also develop. Topf,[13] after subjecting these changes to exact investiga-

[1] *J. Chem. Soc.*, 1898, **73**, 148.
[2] *Chem. Zeit.*, 1895, **19**, 2.
[3] *Z. anal. Chem.*, 1877, **17**, 477.
[4] *Analytical Chemistry*, 5th edition, 1919, vol. ii., p. 648.
[5] *Chem. Centr.*, 1897, **1**, 1169.
[6] *Z. anorg. Chem.*, 1898, **16**, 99.
[7] *Z. anal. Chem.*, 1885, **24**, 546.
[8] *J. prakt. Chem.*, 1868, **103**, 351.
[9] *Ber.*, 1884, **17**, 642.
[10] *Chem. Zeit.*, 1895, **19**, 3.
[11] *Z. angew. Chem.*, 1898, **11**, 951.
[12] *Ibid.*, 1903, **16**, 317; 1905, **18**, 1516.
[13] *Z. anal. Chem.*, 1887, **26**, 150.

tion, recommends that the solution be prepared with well-boiled water, free from carbon dioxide and stored in a cool place, protected from direct sunlight; a small quantity of potassium carbonate (*not* ammonium carbonate) should be added, but this necessitates addition of free acid to the iodine solution, when titrating.

Treadwell[1] states that all difficulties, due to the presence of carbon dioxide, etc., in preparing and storing thiosulphate solutions, may be overcome by dissolving the "pure" commercial salt in distilled water (even if it contains carbon dioxide) and allowing it to stand for eight to fourteen days before standardising. The carbon dioxide thus exhausts its action, a corresponding amount of sulphur separates, and the solution can then be kept for months without undergoing appreciable change. Ammonium carbonate should on no account be added to the solution.

Plimpton and Chorley[2] have recommended the use of barium thiosulphate for iodimetry; it is a very difficultly soluble salt. Mutniansky[3] has pointed out that a solution of this salt, saturated at $17^{\circ}{\cdot}5$, is exactly centinormal.

Arsenious Acid

An alkaline solution of arsenious oxide is unaffected by oxygen, but reacts with chlorine as follows:—

$$As_2O_3 + 4Cl + 5H_2O = 4HCl + 2H_3AsO_4.$$

Bromine and iodine act similarly, in alkaline solution. Hence arsenious acid solution may often be used in place of sodium thiosulphate in conjunction with iodine; it has the advantage of being quite permanent. Its chief application is to the estimation of available chlorine in bleaching powder and in alkaline hypochlorites, the end-point of the reaction being ascertained by spotting on starch-iodide paper (*cf.* Bleaching powder, p. 604).

Pure, powdered, commercial arsenious oxide is used in preparing this solution; it should always be tested by subliming a small quantity from a dish on to a watch-glass; the first portion of the sublimate should not be yellowish, which would indicate the presence of the more easily volatile arsenious sulphide, and the whole should volatilise completely on heating more strongly. The oxide should be dried in the exsiccator over sulphuric acid for some time before use; it may then be weighed out without special precautions, as it is not hygroscopic.

To prepare a decinormal solution, exactly 4·948 g. arsenious oxide is weighed out and boiled with 10 g. pure sodium bicarbonate and

[1] *Analytical Chemistry*, 5th edition, 1919, vol. ii., pp. 645 and 649.
[2] *J. Chem. Soc.*, 1895, 67, 315.
[3] *Zeit. anal. Chem.*, 1897, 36, 220.

200 c.c. water, till completely dissolved; 10 g. of sodium bicarbonate is then added, the solution allowed to cool and diluted to 1 litre.

The solution keeps perfectly; 1 c.c. is equivalent to 0·003546 g. chlorine, or 0·012692 g. iodine.

This solution will be of correct strength, provided pure dry arsenious oxide is used. It may be standardised, however, against pure iodine, exactly as described on p. 69, for sodium thiosulphate, and this check should not be omitted when a large quantity of solution is prepared.

Lunge[1] has shown that sodium arsenite and sodium thiosulphate give identical results and are equally applicable.

Silver Nitrate and Ammonium Thiocyanate

Silver nitrate solution is employed for the volumetric estimation of chlorides, by precipitation as silver chloride, using potassium chromate or sodium arsenate as indicator, in those cases in which rapidity is of greater importance than extreme accuracy; it is also applied to the estimation of cyanides. The method was introduced by F. Mohr. The preparation of this solution is extremely simple, as commercial crystallised silver nitrate is dry and chemically pure, and only requires to be dried in the desiccator, as a precaution, before being weighed out. A decinormal solution is obtained by dissolving 16·989 g. silver nitrate and making up to a litre; 1 c.c. of this solution is equivalent to 0·003546 g. Cl, 0·003647 g. HCl, 0·005846 g. NaCl, etc.

A solution equivalent to 0·001 g. NaCl per c.c. is sometimes preferred; this is obtained by dissolving 2·907 g. silver nitrate per litre of solution.

The solutions to be estimated must not contain any free acid; if this is present, it must be neutralised by sodium carbonate. A slight excess of carbonate is immaterial, whilst the least excess of acid interferes with the reaction. Four to five drops of a cold, saturated solution of normal (yellow) potassium chromate are added to the chloride solution, and the silver solution is then run in, with vigorous stirring, until the white precipitate has acquired a reddish colour, which does not disappear on stirring; the colour is seen even better by artificial light than in daylight, as the yellow colour of the solution is not apparent, whilst the red of the precipitate persists. With a decinormal silver nitrate solution an excess of about 0·2 c.c. is required; this amount must be subtracted from the quantity of solution used. The colour change is sharper when sodium arsenate is used as indicator, and a correction for excess is unnecessary. A titration which has been carried too far can be corrected by addition of $N/10$ sodium chloride solution.

[1] *Z. angew. Chem.*, 1904, 17, 233.

Volhard's[1] method permits the use of acid solutions. A solution of ammonium thiocyanate is required in addition to *N*/10 silver nitrate; this is prepared by dissolving 7·5 to 8 g. of the salt, which is always moist, in 1 litre of solution and accurately adjusting it to the silver nitrate solution. Once standardised, the titre remains perfectly constant. A solution of iron alum (ferric ammonium sulphate), saturated at the ordinary temperature, serves as indicator; 5 c.c. of this are added to from 200 to 300 c.c. of the solution to be titrated. To fix the strength of the thiocyanate solution, 10 or 20 c.c. silver nitrate solution are diluted with 200 c.c. water, and 5 c.c. iron alum solution are added; if a colour develops, nitric acid is added until it disappears. The thiocyanate solution is then run into the silver solution, with continual stirring; the appearance of a light-brown coloration indicates the end-point of the reaction, and its observation is facilitated by the coagulation of the silver thiocyanate. Henriques has pointed out that the thiocyanate must always be run into the silver solution, not *vice versa*. The thiocyanate solution thus tested is corrected and made up to decinormal strength, as described on p. 50. For chloride estimations, the solution to be analysed is treated with *N*/10 silver nitrate until all the chlorine is precipitated as silver chloride and excess of silver nitrate is present; iron alum is then added and the excess of silver titrated back with *N*/10 thiocyanate. The amount of chloride is given by the difference between the volumes of silver nitrate and of thiocyanate solutions used.

IV.—GAS-VOLUMETRIC ANALYSIS

Gas-volumetric analysis, as distinct from gas analysis, comprises those operations in which a constituent of a solid or liquid substance is determined by the generation and measurement of a gas. The gas is usually evolved by the decomposition of the substance under examination; for instance, carbon dioxide from limestone, nitrogen from ammonium salts, nitric oxide from nitrates, oxygen from peroxides, etc.; sometimes, however, it is partially or entirely generated from the reagent used, as in the valuation of hydrogen peroxide by potassium permanganate. In some instances, air displaced by the generated gas is measured instead of the latter.

The description of the methods and forms of apparatus proposed for gas-volumetric work is, in this section, restricted to such as are employed for a number of different purposes and are in general laboratory use. Those forms of apparatus which are either used only for a special purpose, or in a particular industry, are described in the corresponding sections.

[1] *Annalen*, 1878, **190**, 49.

The Azotometer.

This instrument was designed by Knop[1] for the determination of ammonia by the decomposition of its salts with sodium hypobromite, and measurement of the liberated nitrogen. It has been improved in several respects, especially by P. Wagner,[2] and can be used for other

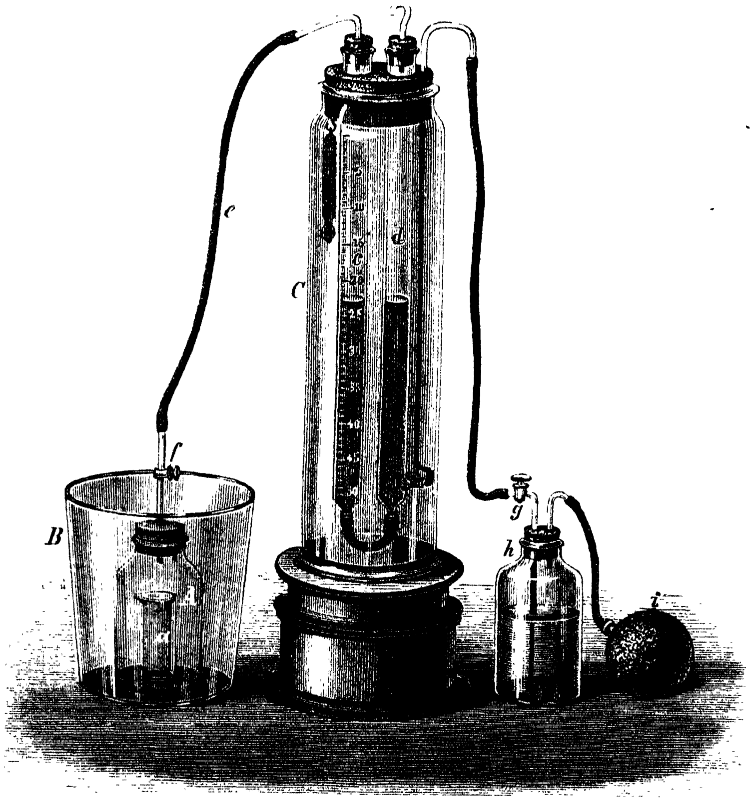

FIG. 21.

gas-volumetric purposes in which measurements are made over water.

The apparatus is shown in Fig. 21. A is a generating vessel for holding the hypobromite solution. This is prepared as follows:—100 g. sodium hydroxide are dissolved in water and diluted to 1·25 litres, 25 c.c. bromine are added, with external cooling by water, the whole well shaken, and finally cooled. The solution is kept in the dark in a

[1] *Chem. Centr.*, 1860, 5, 244. *Z. anal. Chem.*, 1874, 13, 383; 1876, 15, 250.
[2] *Z. anal. Chem.*, 1870, 9, 225; 1875, 14, 247.

well-stoppered bottle. The glass cylinder *a*, of about 20 c.c. capacity, is fused on to the bottom of A, and serves to hold the solution of the ammonium salt. The large glass vessel B is for cooling the generating vessel to its original temperature, after the decomposition. The neck of the generating vessel is rough-ground inside, so as to give a good hold for the rubber stopper, which must be pressed in tightly, and must not slip. C is a tall cylinder filled with water (to which a little hydrochloric acid is added to prevent the growth of moulds), and closed by a cork in which the communicating burettes, *c* and *d*, are fixed; it also carries a small thermometer. The burettes and their supply vessel *h* are filled with water, which may be slightly coloured to facilitate the reading.

To carry out an estimation of ammoniacal nitrogen, 10 c.c. of the ammonium salt solution under examination are introduced into the inner vessel *a*, and 50 c.c. of hypobromite solution into the outer vessel A, by means of a funnel. The rubber stopper is then tightly inserted and the vessel placed in B, which is filled with water. The glass tap *f* is loosened slightly, water introduced into the burettes *c* and *d* by squeezing the rubber ball *i* and opening the tap *g*, and then run off through *g* down to the zero mark of the burette. After about ten minutes the cock *f*, which is slightly greased, is inserted tightly, but left open so that A and *c* are in communication. If, after an interval of five minutes, the liquid in *c* has risen, the cock *f* is again loosened, re-inserted tightly, and the apparatus again allowed to stand for five minutes. If the liquid has remained at the zero mark, the temperature of the generating vessel and contents has become equal to that of the surrounding water, and no more carbon dioxide from the enclosed air is being absorbed by the hypobromite solution.

For the decomposition, 30 to 40 c.c. of water are first withdrawn from the burette through *g*, and the generating vessel removed from B and tilted, so that a small portion of the contents of *a* flows into the hypobromite solution, with which it is mixed by gentle shaking. This is repeated until the greater portion of the ammoniacal liquid has been poured out and decomposed. The tap *f* is then closed, the generating vessel thoroughly shaken, *f* again opened to allow any liberated nitrogen to pass to the burette, and this repeated until the liquid in *c* remains at a constant level; shaking three times is usually sufficient. The generating vessel A is then replaced in B; fifteen to twenty minutes suffice for this vessel and its contents to acquire the temperature of the surrounding water and for the gas in *c* to reach that of the water-jacket C, which is indicated by the thermometer. The tap *g* is then opened until the water is at the same level in *c* and *d*, and the volume of liberated nitrogen, the temperature of the water in

C, and the barometric pressure noted. The weight of nitrogen may then be calculated. The decomposition is, however, incomplete, possibly owing to the formation of hydrazine.[1]

Lunge[2] has shown that an addition of 2·5 per cent. to the volume of gas found is a satisfactory compensation factor for this source of error. On this basis 1 c.c. N_2 at 0° and 760 mm. (dry) = 0·001558 g. NH_3. This factor is calculated from the observed density of nitrogen.

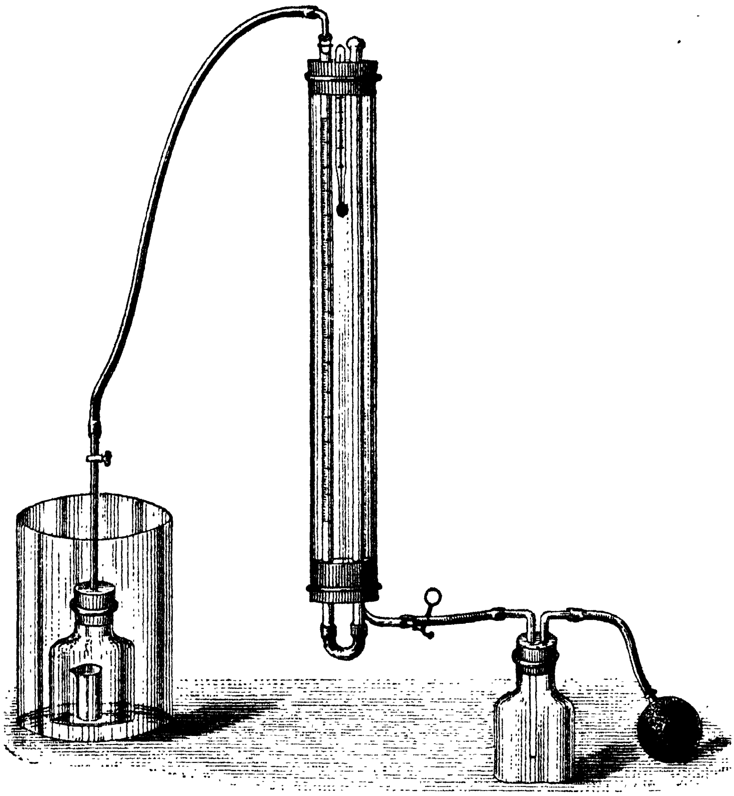

FIG. 22.

A. Baumann recommends the simplified form of Wagner's Azotometer shown in Fig. 22, for technical laboratories, in which the measuring tube is replaced by an ordinary pinch-cock burette; the manipulation of the apparatus is in all respects similar to that described above. If many analyses have to be performed it is well to keep two or three such simplified azotometers in use, so as to save time whilst the original temperature is being attained after the decompositions.

[1] Raschig, *Chem. Zeit.*, 1907, **20**, 206. [2] *Chem. Ind.*, 1885, **5**, 165.

The Nitrometer.

The name "Nitrometer" was given by Lunge[1] to the apparatus he devised for the determination of nitrogen acids, by decomposition with sulphuric acid in presence of mercury. This reaction was made use of long ago by W. Crum[2] for the analysis of nitrates and of gun-cotton, and subsequently, in an improved form, by Frankland and Armstrong[3] for the determination of nitrates in water, and by G. E. Davis[4] for the valuation of nitrous vitriol, but manipulative difficulties restricted its applicability; the nitrometer has rendered the reaction thoroughly practicable, and has thus been the means of bringing it into general use.

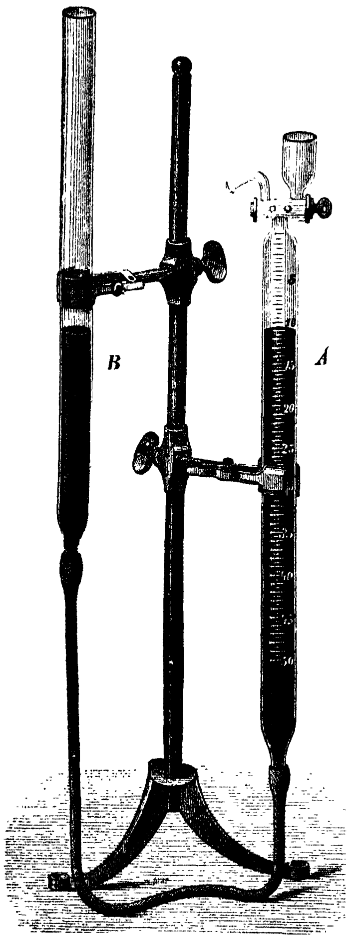

FIG. 23.

In the method as originally devised, the mercury over which the gas is collected also takes part in the reaction. It has since been extended to many other purposes, in which the mercury does not take part in the decomposition, but serves simply as the confining liquid for the liberated gas, and also to determinations in which the decomposition is effected in a separate vessel and the evolved gas collected and measured in the nitrometer.

The nitrometer is shown in Fig. 23 in the form used most for the analysis of nitrous vitriol in the sulphuric acid industry, and for many other purposes. The tube A has a capacity of 50 c.c.; it is drawn out at the bottom and is graduated in $\frac{1}{10}$ c.c. The graduations start

[1] *Ber.*, 1878, **11**, 174; 1885, **18**, 1878 and 2030 (New applications); 1888, **21**, 376. *Dingl. polyt. J.*, 1879, **231**, 522 (Tables); 1882, **245**, 171 (Analysis of dynamite). *Chem. Ind.*, 1881, **4**, 346; 1885, **8**, 161 (New applications); 1886, **9**, 273 (Analysis of explosives). *J. Soc. Chem. Ind.*, 1882, **1**, 15; 1885, **4**, 495; 1886, **5**, 82; 1888, **7**, 232; 1892, **11**, 778. *Sulphuric Acid and Alkali*, 2nd edition, 1891, p. 182. *Cf.* also A. H. Allen, *J. Soc. Chem. Ind.*, 1885, **4**, 178.

[2] *Phil. Mag.*, 1847 [iii.], **30**, 426.

[3] *J. Chem. Soc.*, 1868, **21**, 101.

[4] *Chem. News*, 1878, **37**, 45.

immediately below the three-way tap which terminates the tube at the top. This tap may either have a vertical and an axial passage, or it may be a Friedrich-Greiner tap with two oblique passages, as shown in its three positions in Fig. 24. The latter form closes more tightly and is more easily manipulated than the former, and is therefore used in the newer forms of the apparatus. Above the tap, a beaker and a side tube *d* are attached; the latter replaces the axial passage of the older form of tap. In position A the measuring tube communicates with the side tube *d*, in position B with the beaker, and in position C the tap is closed.

The measuring tube A (Fig. 23) is connected by means of thick-walled rubber tubing with the pressure tube B. The latter is a simple cylindrical glass tube of the same diameter as the measuring tube, and drawn out at

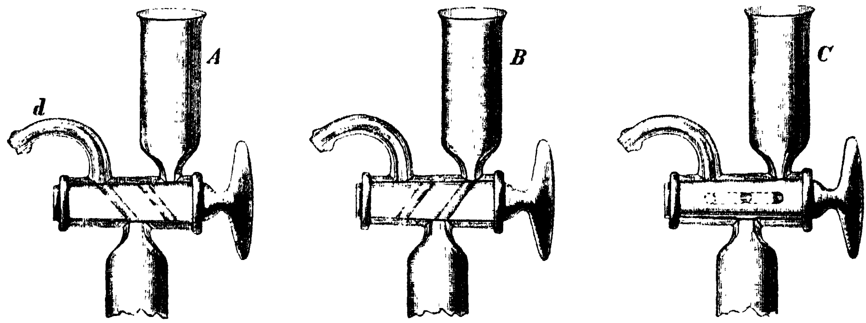

FIG. 24.

the bottom for the attachment of the rubber tubing. Both tubes are held by clamps, in which they can be moved.

To use the apparatus, for instance for the assay of nitrous vitriol, the tube B is placed so that its lower end is somewhat higher than the tap on A, and mercury is poured in through B, the tap on A being open, until it just enters the beaker on A; as the mercury enters A from below, no air-bubbles are formed on the sides of the tube. The tap is then closed and the pressure tube lowered.

The nitrous vitriol is then introduced into the beaker from a 1 c.c. pipette divided into $\frac{1}{100}$ c.c.; in the case of very strong nitrous vitriol 0·5 c.c. are used, in other cases 2 to 5 c.c. The pressure tube B is then lowered, the tap carefully opened, and the acid drawn into the measuring tube, care being taken not to admit any air. The beaker is then rinsed with 2 to 3 c.c. of sulphuric acid, free from nitrogen acids, which is similarly drawn into the measuring tube, and the washing repeated with 1 to 2 c.c. more of sulphuric acid. The decomposition is then started by removing the tube A from its clamp, and thoroughly mixing the acid and mercury by repeatedly holding the tube almost horizontally, taking care that no acid gets into the

rubber tubing, and then sharply raising it to a vertical position. The tube is shaken for one to two minutes until no more gas is evolved.

The two tubes are then placed so that the mercury in B is as much higher than that in A as is necessary to compensate for the layer of acid in the latter; 1 mm. mercury is allowed for every 6·5 mm. of acid. After the temperature has become equalised the pressure is exactly adjusted by pouring a little acid into the beaker and opening the tap cautiously. If the gas is under diminished pressure, which is preferable, acid will flow into A; the tap is at once closed before air can enter, and the operation repeated after raising the pressure tube very slightly. If, on the contrary, the enclosed gas tends to force its way through the acid, the tap is closed, the pressure tube lowered slightly, and the tap again opened. With a little care these manipulations can always be successfully carried out. The volume of the gas, the barometric pressure, and the temperature are then read; the latter by means of a thermometer, the bulb of which is placed close to the measuring tube and near the middle of the column of gas.

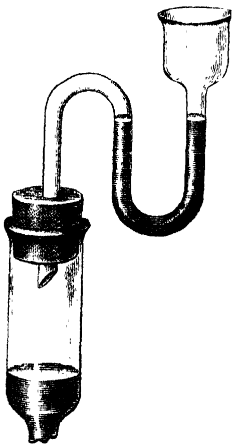

FIG. 25.

When the determination is finished the measuring tube A is lowered, so that no air may enter on opening the tap, and the gas expelled by raising the pressure tube. The acid is expelled, either through the side tube *d* (Fig. 24), or through the axial passage in the older form of tap, and the last traces removed with filter paper. The nitrometer is then ready for the next determination. Details with regard to the calculation of the amount of nitrogen compounds from the volume of gas obtained are given in the section on "Sulphuric Acid."

The analysis of nitrates or of nitrites soluble in water, to determine the total nitrogen, is carried out similarly, as is described in the analysis of sodium nitrate. Where a solid soluble in water is to be analysed, the weighed substance is introduced into the beaker, dissolved there in a very small quantity of water, the solution drawn into the measuring tube, the beaker rinsed with concentrated sulphuric acid, and the decomposition carried out as described.

In the analysis of substances insoluble in water but soluble in strong sulphuric acid, more especially dynamites and pyroxylins, for which purpose the nitrometer is now almost always used, the solution in sulphuric acid is also carried out in the attached beaker. In order to avoid loss of nitrous fumes, the device shown in Fig. 25, due to Lunge,[1] is used. The beaker of the nitrometer is closed

[1] *Chem. Ind.*, 1886, 9, 274.

by a rubber stopper provided with an S-tube, ending above in a small funnel. The substance is placed in the beaker, and concentrated sulphuric acid introduced through the funnel. The lower bend of the tube naturally remains full of sulphuric acid, which prevents the escape of nitrous fumes, and which flows into the beaker, as the acid in the latter is drawn into the measuring tube.

It is immaterial whether an insoluble powder, such as kieselguhr in the case of dynamite, or some undissolved saltpetre, etc., remains, as this is sucked into the measuring tube with the liquid; in the analysis of pyroxylin it is, however, better to wait till it has completely dissolved in the beaker.

Nitrates and esters of nitric acid, such as nitroglycerine and nitrocellulose, can be analysed in the apparatus shown in Fig. 23, but a high degree of accuracy is not obtainable, as not more than 40 c.c. of gas can be measured. By using a modified form, the "nitrometer for saltpetre," shown in Fig. 26, an accuracy of 0·1 per cent. may be obtained in these determinations. In this form a larger space for gas is provided without making the apparatus inconveniently long, by means of a bulb of nearly 100 c.c. capacity, below which the graduations extend from 100 c.c. to 130 c.c.

In Fig. 27 a form of nitrometer is shown which may be used for determinations in which either a small or a large volume of gas is evolved. As it cannot be made as short as the forms shown in Figs. 23 and 26, it is not so suitable for shaking, but it is well adapted for use in conjunction with a decomposition bottle or as a gas-volumeter (cf. *infra*).

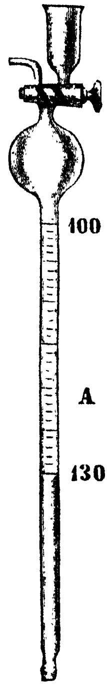

Fig. 26.

Fig. 27.

When nitrous and nitric acid compounds are decomposed by shaking in the measuring tube itself with mercury and sulphuric acid, a layer of sulphuric acid finally remains between the gas and the mercury, which has to be allowed for in adjusting the pressure for the final measurement, as stated above. This causes no special difficulty as a rule, but when considerable quantities of substance are decomposed, much frothing sometimes occurs; on dilution with water, which is sometimes unavoidable, sulphate of mercury is precipitated, and in the analysis of dynamite the kieselguhr floats on the acid, etc. These factors make the final adjustment and measurement uncertain and inexact. It is therefore advisable, for instance in the analysis of saltpetre and of explosives, to use a separate decomposition vessel, with an attached

pressure tube, as in the gas-volumeter. The gas is then always measured over a sharp meniscus, and the volume can be read with the greatest accuracy.

The same considerations apply to all those methods of analysis in which the nitrometer is used in conjunction with an attached decomposition bottle, as shown in Fig. 28. The substance to be decomposed is placed in the outer annular space, and the decomposing agent in the inner vessel, which is fused on to the bottom of the bottle. After replacing the stopper, the bottle is connected with the tap of the nitrometer, the measuring tube of which has been completely filled with mercury ; the stopper is again loosened, to make sure that there is no excess of pressure in the generating bottle, and the mercury in the nitrometer readjusted to zero, if necessary, by moving the pressure tube. The tap of the nitrometer is then turned so as to connect the

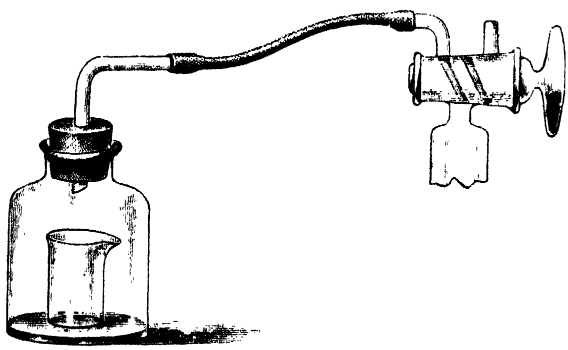

FIG. 28.

measuring tube and the generating bottle, and the latter tilted, so that the liquid in the inner vessel flows into the surrounding space. In doing this care must be taken that the bottle is not warmed by the hand, and this applies also to the subsequent shaking to promote the disengagement of the gas ; it is safest, especially if heat is evolved, as in decompositions by the sodium hypobromite method, to place the generating bottle up to the neck in a beaker of water, before and after the reaction. As the mercury in the measuring tube is depressed by the evolved gas, the pressure tube is lowered accordingly, to prevent any excessive pressure ; it is sometimes advantageous to lower the pressure tube considerably towards the end of the reaction, in order to facilitate the removal of the gas. After the original temperature has been attained the mercury is brought to the same level in both tubes, and the volume of the gas read, together with the temperature and pressure.

In reducing to 760 mm. pressure, it must be borne in mind that the gas is moist, and not dry, as is usually the case in working with a

nitrometer; since it is always generated from dilute solutions, the tension of the water-vapour may be considered equal to that of pure water at the same temperature.

The reduction of the volume of gas to normal volume is calculated most easily by means of the Tables II. to IV., appended to this volume, which were specially compiled for use with the nitrometer by Lunge; the calculation can also be done by reversing the formulæ on p. 85.

The numerous applications of this form of the nitrometer include the valuation of potassium permanganate solution (p. 66), the analysis of bleaching powder, manganese dioxide, potassium ferricyanide, lead peroxide, nitrous acid,[1] hydrogen peroxide, the determination of carbon dioxide in carbonates (preferably by Lunge and Marchlewski's method), of nitrogen in ammonium salts, in urea (ureometer), and in diazo-compounds, the control of the strength of acids by liberation of carbon dioxide from carbonates, the valuation of zinc-dust, the examination of chromates[2] and the titration of iodine solutions.[3]

The nitrometer can also be used as an absorptiometer,[4] as an apparatus for reducing the volume of gases to 0° and 760 mm. pressure,[5] although the gas-volumeter is far preferable for this purpose, and for gas analysis work;[6] also for the collection and analysis of gases dissolved in water, etc.[7]

The Gas-Volumeter.[8]

This name was given by Lunge to an apparatus, by means of which the reduction of a volume of gas, either wet or dry, to any required normal conditions, usually, of course, to 0° and 760 mm. pressure, is effected without observation of the temperature and pressure, and without calculation or reference to tables.

The principle of the apparatus is to enclose a known volume of air, at such a pressure that it takes up exactly the volume which it would occupy at 0° and 760 mm. pressure. If the same pressure and temperature are then applied to another volume of gas, this will also take up the volume which it would occupy at 0° and 760 mm. pressure. This condition is attained by confining the known volume of air in a "reduction tube" to which a pressure tube is attached, and placing the latter in such a position that the gas in the reduction tube is brought to the volume it would occupy under normal conditions;

[1] Riegler, *Z. anal. Chem.*, 1897, **36**, 665.
[2] A. Baumann, *Z. angew. Chem.*, 1891, **4**, 135, 198, 339, 392.
[3] *Z. angew. Chem.*, 1891, **4**, 203, 328, 450.
[4] *Chem. Ind.*, 1885, **8**, 162.
[5] *Chem. Ind.*, 1885, **8**, 163.
[6] *Ibid.*, 1885, **8**, 169.
[7] *Ibid.*, 1885, **8**, 170; *Z. anal. Chem.*, 1886, **25**, 309.
[8] Lunge, *Ber.*, 1890, **23**, 440; 1892, **25**, 3157. *Z. angew. Chem.*, 1890, **3**, 139; 1891, **4**, 197, 410; 1892, **5**, 677. *J. Soc. Chem. Ind.*, 1890, **9**, 547.

the reduction tube is also connected with the gas measuring tube by means of a T-piece, and by adjusting the level of the mercury in the two tubes to the same height, the volume correction is applicable directly to the gas in the measuring tube.

The apparatus is shown in Fig. 29. The three tubes, A, B, and C, are connected by means of a T-piece and sufficiently long thick rubber

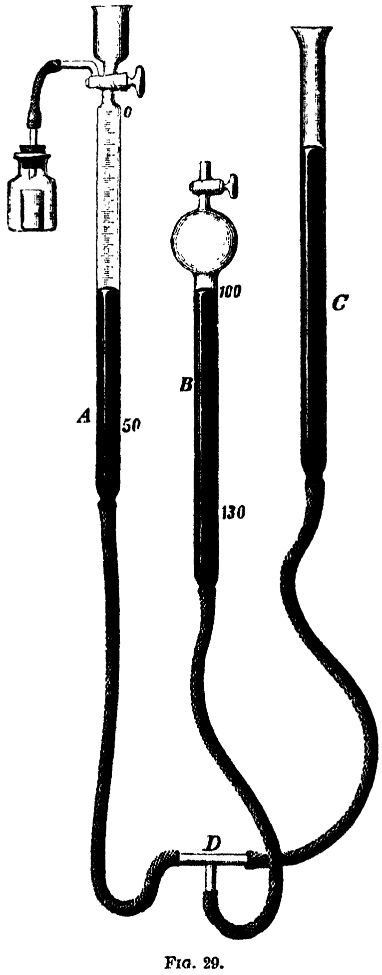

Fig. 29.

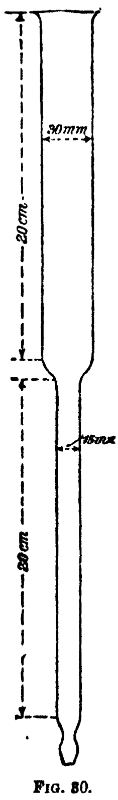

Fig. 30.

tubing, and are held to a stand by clamps, in which they can be moved in a vertical direction. The tube A is the measuring tube, and may be a nitrometer of any form, a Bunte burette, or any other apparatus for the measurement of gases. The second tube, B, the so-called reduction tube, is enlarged to a bulb at the top; the first graduation is below the widened portion of the tube, and indicates a volume of 100 c.c., and the lower cylindrical portion of the tube is graduated

in $\frac{1}{10}$ c.c. for another 30 to 40 c.c. The tube is set, once for all, by observing the temperature and pressure, calculating the volume which 100 c.c. of dry air would occupy under the observed conditions, bringing the mercury to the corresponding division, and closing the tap above the bulb. If the tap is air-tight the reduction to 0° and 760 mm. pressure has been permanently made; an alternative is to provide the upper end of the tube with a capillary, which can be sealed off, after the volume has been correctly adjusted.

This form of reduction tube was subsequently modified by Lunge and replaced by a cylindrical tube in order to bring the volumes of enclosed gas as far as possible into a parallel position, and the pressure tube, C, by the form shown in Fig. 30, which requires less mercury.

If moist gases are to be measured in the measuring tube, a small drop of water must be introduced into the reduction tube; if dry gases are to be measured, *e.g.*, nitric oxide generated over sulphuric acid in the ordinary nitrometer, a drop of concentrated sulphuric acid is introduced into the reduction tube, but never in sufficient amount to more than cover the top of the mercury meniscus. The gases must be measured either quite dry or saturated with moisture.

Formula for dry gases: $$V_1 = V_0 \frac{(273+t)760}{273 \times B}$$

Formula for moist gases: $$V_1 = V_0 \frac{(273+t)760}{273(B-f)}$$

Where V_1 = Volume of gas required.
V_0 = Normal volume of gas.
t = Observed temperature.
B = Observed barometric pressure.
f = Tension of water-vapour at observed temperature.

To adjust the reduction tube, the temperature is observed by means of a thermometer suspended by the side of the tube, and the barometric pressure read. The volume V_1 which 100 c.c. of gas at normal temperature and pressure V_0 will occupy at the observed temperature and pressure, either dry or moist, is then calculated, either by means of the above formulæ or from the Tables II. to IV. appended to this volume. The pressure tube is then adjusted, so that the mercury in the reduction tube is at the calculated graduation, and the tap closed. The instrument is then ready for use.

Dry gases can, if desired, be measured with a wet reduction tube, or *vice versa*. In the former case the temperature is observed, the corresponding vapour-tension f in mm. found from Table IV., and the mercury in the measuring tube placed f mm. higher than in the reduction tube, after the volume in the latter has been adjusted to 100 c.c. This is facilitated by using measuring tubes in which each c.c. of

the graduation corresponds almost exactly with 10 mm. length, as the use of a measuring scale is thereby avoided. When a dry reduction tube is used for moist gases, the mercury in the measuring tube must be placed f mm. lower than in the reduction tube, in which the volume has been adjusted to 100 c.c.

An alternative plan for comparing dry gases with a moist reduction tube is to moisten the gas in the measuring tube by drawing in a drop of water; this is preferably done before the gas is collected, but it can also be done afterwards with careful manipulation; for the reverse comparison a drop of concentrated sulphuric acid is used. In neither case must more liquid be added than covers the top of the mercury meniscus.

The three tubes, A, B, C (Fig. 29), are connected with the T-piece D by very thick-walled rubber tubing of 13·5 mm. external and 4·5 mm. internal diameter, which withstands the pressure of the mercury without being distended and does not need binding with wire, especially if the ends of the tubes are enlarged a little; it is easily drawn over tubes of 10 mm. or greater diameter. All three tubes are held in strong clamps, so that they may be moved vertically with friction, but do not drop down by their own weight.

When any gas-analytical or gas-volumetric operation has been carried out in A, the volume of gas is not read in the ordinary manner, after adjusting the mercury in A and C to equal levels. This adjustment is only made as a preliminary step when an auxiliary generating bottle is used, as in decompositions by sodium hypobromite or hydrogen peroxide, or in carbon dioxide determinations, etc.; in these cases the mercury levels in A and C must first be equalised, in order to bring the gas in A to the ordinary atmospheric pressure. The tap of A is then closed, without reading off the volume of contained gas. If the gas has been generated in A itself, or has been transferred from another vessel, this adjustment is of course unnecessary. Before actually reading the volume of gas in A, the three tubes are so adjusted that the mercury in B stands at the 100 c.c. graduation and the levels in A and B are the same. The gas volumes in A and B then correspond to such temperature and pressure that their volumes are equal to those which they would occupy, when dry, at 0° and 760 mm. pressure, since this condition has been ensured once for all in the case of B, and the gas in A is at the same temperature and the same pressure.

The required adjustment is most quickly and easily carried out in the following manner. The tube A is fixed in its clamp whilst B and C are raised, C to such an extent that the mercury in B rises to the graduation 100 c.c.; B and C are then lowered simultaneously, so that the difference of level of the mercury in the two tubes is maintained, until the mercury stands at equal levels in A and B, in the latter still at

the 100 c.c. graduation. The adjustment will usually be found to be not quite exact, and a slight movement of B will probably be necessary to complete it, but this double adjustment only requires a few seconds longer than the ordinary adjustment of the pressure tube of a gas-burette.

The simultaneous movement of the reduction and pressure tubes is advantageously effected by the use of a forked clamp such as that shown in Figs. 31 and 32.

This consists of two cork-lined clamps supported by a cast-iron fork. The smaller clamp *a* holds the reduction tube (below the 100 c.c. graduation), and the larger, *b*, the pressure tube. The fork is fastened to the stand by means of an ordinary boss *c*, shown on a larger scale in Fig. 32, which may be strengthened by a spring. After the gas-analytical operation is finished, the adjustment is made by first bringing the reduction and pressure tubes to the approximate level of the mercury in the measuring tube. The pressure tube is then moved in its clamp *b*, until the mercury in the reduction tube stands exactly at the 100 c.c. graduation. The forked clamp is then moved as a whole, by means of the boss *c*, until the mercury levels in the reduction and measuring tubes are equal. The whole adjustment only takes a few seconds, and is much easier than when separately movable clamps are used.

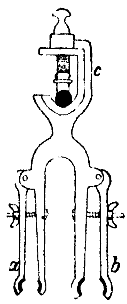

FIG. 31.

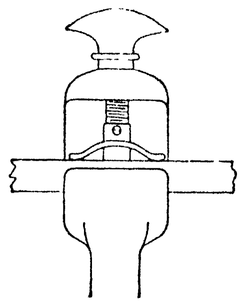
FIG. 32.

Lunge[1] has devised a mechanical stand, which is extremely convenient for manipulating the gas-volumeter, and which is applicable to all forms of the nitrometer.

Special forms of the gas-volumeter have been designed by Lunge,[2] for the determination of nitrogen in elementary organic analysis, and by Lunge and Neuberg[3] for the determination of vapour densities.

When the gas-volumeter is in daily use for a specific determination, the graduations on the measuring tube may be made to correspond with definite weights in mg. of the constituent determined, or to percentages, when a definite weight of initial material is taken for analysis. Such graduations may either replace the divisions into c.c. or may be placed alongside them.

Special graduation of the measuring tube is unnecessary, if the quantities given in the following table are used for analysis; an ordinary measuring tube, divided into $\frac{1}{10}$ c.c., can then be employed.

[1] *Z. angew. Chem.*, 1892, **5**, 678. [2] *Ber.*, 1890, **23**, 446. [3] *Ibid.*, 1891, **24**, 729.

Table for the Conversion of Volumes of Gas, obtained in the Gas-Volumeter, into Weights of Active Constituents.

1	2	3	4	5
Substance Analysed.	Active Constituent.	Method of Analysis.	Gas Evolved.	1 c.c. Gas = Active Constituent in mg.
Organic substances.	Nitrogen	Dumas' method	N_2	1·2507
Ammonium salts	Do.	With sodium hypobromite	N_2	1·2819[1]
Do.	Ammonia	Do.	N_2	1·5582[1]
Urine	Urea	Do.	N_2	2·956[1]
Bone-charcoal, marl, etc.	Carbon dioxide	Decomposition by HCl	CO_2	1·9768
Do.	Calcium carbonate	Do.	CO_2	4·4968
Pyrolusite	Manganese dioxide	With H_2O_2	O_2	3·8825
Bleaching powder	Chlorine	Do.	O_2	3·1675
Potassium permanganate	Oxygen	Do.	O_2	0·7146
Chili saltpetre	Sodium nitrate	In nitrometer	NO	3·7986
Nitrous vitriol	N_2O_3	Do.	NO	1·6974
Do.	HNO_3	Do.	NO	2·8143
Do.	Nitric acid of sp. gr. 1·33	Do.	NO	5·3771
Do.	Sodium nitrate	Do.	NO	3·7963
Nitroglycerine, dynamite, etc.	Trinitroglycerine	Do.	NO	3·358
Do.	Nitrogen	Do.	NO	0·6257
Nitrocellulose, pyroxylin	Do.	Do.	NO	0·6257

[1] These values are corrected for the "nitrogen absorption"; 2.5 per cent. in the case of ammonium salts, and 9 per cent. in the case of urea. (*Cf.* p. 77.)

The table comprises a number of substances, specified in the first column, which are frequently examined by gas-volumetric methods. The second column gives the "active constituent" of the substance analysed; the third column, the analytical method employed; the fourth, the nature of the evolved gas; the fifth, the weight of "active constituent" in mg. corresponding to 1 c.c. of dry gas at 0° and 760 mm. pressure. If one hundred times the quantity of substance given in column 5 is taken, then the number of c.c. of gas obtained is numerically equal to the percentage of the active constituent. In some cases it is necessary to use a larger quantity of substance, and then 1 c.c. of gas represents, of course, a correspondingly smaller percentage.

The data given in this table are based on the observed densities of the gases concerned, not on the values calculated from the molecular weights, which do not take into account the deviations from Boyle's law.

Japp[1] has shown, that by suitably adjusting the position of the reduction tube, the volume of gas in the measuring tube may be made to indicate the weight of active substance present, without further

[1] *J. Chem. Soc.*, 1891, **59**, 894; *cf.* also Lunge, *Ber.*, 1891, **24**, 1656 and 3491.

calculation and without special graduation. This proposal seldom offers, however, any advantage over the above method of working.

The principle of the gas-volumeter has been applied by Lunge and Marchlewski to the exact estimation of carbon dioxide in carbonates [1] and to that of carbon in iron and steel.[2]

THE CALCULATION OF ANALYTICAL RESULTS

Means which shorten the calculations of analytical results, especially if they also contribute to the avoidance of error, greatly facilitate the work of a technical laboratory. Four-figure logarithms are not sufficiently accurate for most work, as the fourth place is uncertain, but five-figure logarithms almost always suffice. Ready-reckoners are preferred by many, and the slide-rule can be very advantageously used for many technical calculations. Tables specially calculated for chemical purposes are a still more convenient adjunct to analytical calculations.

Published tables are naturally not adapted for every class of work, and it is often convenient to prepare special tables of factors for specific calculations such as those given in the section on "Sulphuric Acid," or for use with the nitrometer (p. 88).

It is a general rule, in both scientific and technical analysis, to calculate to one, and only one figure beyond that which can be regarded as significant. If a method is reliable to within one-tenth per cent., the percentage results should be given to not more than two places of decimals. If, however, an ore is valued in percentages only, it is often advisable to give the analytical result in whole percentages, or at most to one-quarter or one-tenth per cent., so as to avoid confusion in the sales.

There are two quite different cases which must not be confused in this connection. If the main constituent of a substance, representing perhaps 50, 80, or 90 per cent. of the total, has to be determined, the percentage will practically never be given to more than two places of decimals, as even the first place will only occasionally be reliable. In most other cases, also, it would be useless, or even misleading, to give the percentage to more than two places of decimals. But where a constituent has to be determined which only occurs in very small amount, such as gold in quartz, phosphorus in steel, ammonia in water, and the like, it is necessary to give the result to a hundredth or even to a thousandth per cent. of the original substance, provided the

[1] *Z. angew. Chem.*, 1891, 4, 229; 1893, 6, 395. *J. Soc. Chem. Ind.*, 1891, 10, 658.

[2] Cf. *Stahl und Eisen*, 1891, 11, 666; 1893, 13, 655; 1894, 14, 624; also, *Z. angew. Chem.*, 1891, 4, 412.

analytical methods employed are sufficiently accurate and a knowledge of the exact quantity is important.

The choice of the atomic weights to be used in calculating the results of analyses is an important consideration. New determinations are constantly being made, and within recent years many fundamental figures, *e.g.* the ratio H : O = 1 : 15·96, which had long been considered absolutely reliable, have been found to need revision; nor can work in this direction be regarded as final. Many chemists were accordingly of the opinion that it would be an advantage to use approximate atomic weights for technical purposes, as these are less likely to be affected by subsequent determinations. The tables prepared by the International Committee on Atomic Weights have removed any objection to the use of the values now regarded as the most accurate. The atomic weights are all calculated on the basis O = 16, as this is the only one likely to be adopted internationally for analytical purposes.

The table opposite is that approved by the International Committee for 1921.

LITERATURE ON VOLUMETRIC ANALYSIS

FRESENIUS, R.—*Quantitive Chemical Analysis*, 7th edition. Vol. i. translated by A. Vacher, 1876; vol. ii. translated by C. E. Groves, 1900

GOOCH, F. A.—*Methods in Chemical Analysis*, 1912.

SUTTON, F.—*Volumetric Analysis*, 11th edition.

TREADWELL, F. P.—*Analytical Chemistry*, translated from the German by W. T. Hall, 5th edition, 1919.

International Atomic Weights (1921).

	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	70·1
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·008
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	45·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·15
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89·33
Zinc	Zn	65·37
Zirconium	Zr	90·6

ELECTROLYTIC METHODS OF CHEMICAL ANALYSIS

By H. J. S. SAND, D.Sc., Ph.D., F.I.C., Head of the Department of Inorganic and Physical Chemistry, The Sir John Cass Technical Institute, Aldgate, London

I.—THE ELECTROLYSIS OF METALLIC SALTS

ELECTROLYTIC methods applied to chemical analysis have rendered many determinations accurate and rapid which are difficult to carry out by ordinary gravimetric and volumetric processes. These methods have in some instances, typically in the case of copper and nickel, been adopted as recognised methods of analysis in technical laboratories, and in others as useful alternative processes to the ordinary analytical procedure. During recent years the applicability of electrolytic methods has been much extended, and the conditions of deposition have been very fully investigated, especially from the standpoint of modern developments of electro-chemistry.

This section consists of an account of the methods available for electrolytic analysis, of the apparatus employed and of the general conditions applicable to the solutions in which the electrolysis is effected. The more specific details of the conditions under which the methods are used in individual estimations will be given in the respective sections, especially in that on Non-ferrous Metals (Volume II.)

As a rule a metal is deposited from a solution of one of its salts on a cathode of platinum or other suitable metal, and weighed. By varying the electrical conditions and the nature of the solution, first one metal and then another may often be precipitated quantitively from a given liquid.

Sometimes, on the other hand, the electric current is employed to bring about changes in the solution adjoining the electrodes, which lead to the precipitation on the latter of insoluble substances suitable for quantitative determination. Thus, when an electric current is passed under suitable conditions through the solution of a salt of

bivalent lead, a deposit of lead peroxide is precipitated on the anode, most probably as a result of the formation of salts of quadrivalent lead in immediate contact with the electrode. In a similar manner manganese may be precipitated as hydrated manganese dioxide and then brought into a condition suitable for weighing. Again, when an electric current is passed through the solution of a molybdate, reduction takes place which leads to the quantitative precipitation on the cathode of hydrated molybdenum sesquioxide.

II.—APPARATUS EMPLOYED IN ELECTROLYTIC ANALYSIS

1. The Current Supply.

Where accumulators are not available, and when only small currents are required, batteries composed of primary cells may be employed. These should be of a non-polarisable type, such as the well-known Daniell or Bunsen cell. Thermopiles are sometimes employed. These can be obtained commercially to give currents of up to about 3 or 4 ampères through an external resistance of about 0·6 ohm, the voltage on open circuit being about 3 to 4 volts. Wherever possible, the use of accumulators is, however, to be recommended on account of the constancy and magnitude of the current that may be obtained from them. Two or three cells connected in series will give a voltage sufficient for most purposes of electrolytic analysis. Where electric lighting or power mains are available, the charging is usually carried out by means of motor-generator sets, which can now be obtained in very small units. It is often found convenient to dispense with secondary batteries altogether and to employ a motor-generator direct, though the steadiness of the current will be somewhat reduced thereby. Where continuous current for lighting is available, a plan frequently adopted, particularly for occasional electrolysis, consists in connecting the electrolytic cell to the mains through a back-resistance. Though the latter may be of any of the usual types, suitably chosen in regard to resistance and carrying capacity, the form most frequently used is that of a lamp-resistance. This consists of lamps placed in holders fitted to a wooden base and connected in parallel. Where procurable, old carbon-filament lamps are employed on account of the large current they take. The current is varied by altering the number and size of the lamps. When deciding to work on this plan, the fact must not be forgotten that the voltage required for electrolytic analysis is usually about 4, whereas that of most lighting circuits is about 200, so that approximately 98 per cent. of the power taken from the mains is wasted.

2. Regulation and Measurement of the Current.

In nearly all cases a back-resistance, of which there are many suitable forms, is employed to regulate the current and to prevent short circuits.

Except for routine work in which all the conditions are exactly repeated in each analysis, the current should always be measured. For this purpose an ammeter of the moving-coil type will be found the most convenient to employ. Such an instrument may be briefly described as a technical form of the well-known d'Arsonval galvanometer which has been placed on a suitable shunt. The main advantages of moving-coil instruments are, that they have a practically uniform scale, are always made so as to be dead-beat, and are almost independent of the way in which they are set up; a disadvantage is their slightly greater cost compared with instruments of the so-called "gravity" type.

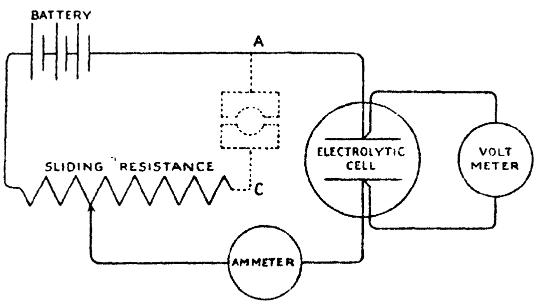

FIG. 33.

The measurement of the voltage between anode and cathode is often found of value. This voltage is the algebraic sum of (1) the potential difference between anode and electrolyte, (2) that between electrolyte and cathode, and (3) that required to force the current through the solution between anode and cathode according to Ohm's law. It will thus be seen that except where (1) and (3) are fairly constant, a condition by no means usually fulfilled in electrolytic analysis, the voltage between the electrodes is not a direct measure of (2), which is the quantity of analytical interest. Justification of its measurement is to be found in the fact that it gives a general idea of the course of electrolysis, and that it is simple to make.

As with ammeters, the best type of voltmeter to employ will probably be found to be one of the moving-coil class. In design these instruments are similar to the ammeters, except that the measuring device is placed in series with a high resistance instead of being put on shunt with a very low one.

Fig. 33, leaving out the dotted portion, illustrates the electrolytic circuit thus far described.

3. Electrolytic Analysis with Control of the Cathode-potential.

As has already been pointed out, the potential difference between anode and cathode is only of indirect interest. Where separations of metals from each other have to be carried out, the potential difference between the cathode and the electrolyte becomes the governing factor. To obtain a correct measure of this, a non-polarisable auxiliary electrode must be employed which is placed outside the lines of flow of the current. If the latter is regulated so that the potential difference between the auxiliary electrode and the cathode is confined between certain definite limits, it is often possible to restrict the action of the current to one single electrolytic process, such as the precipitation of one metal from a solution of several, or to obtain metal only without hydrogen. The fine regulation of the current for this purpose is obtained by connecting the battery-terminals to the two ends of a sliding resistance, and the electrolytic cell to one end of the resistance and to the slider, thus allowing any voltage from zero to the maximum of the battery to be tapped off.

Fig. 33 shows how the circuit just described can, by connecting the points A and C, be converted into one suitable for separations by graded potential. If desired, a plug can be introduced, so that either one or the other arrangement may be employed at will. Resistances of 2 to 3 ohms having a carrying capacity of about 15 ampères have proved suitable. It will be seen that if the voltage at the ends of the resistance is about four, one or two ampères are lost in the sliding resistance in an arrangement of the circuit for separation by graded potential. In suitable cases, the current passing through the electrolytic cell, which may be started at a value of about 3 or 4 ampères, automatically drops to about zero as the metal disappears from solution, a very important and useful indication of the progress of the analysis.

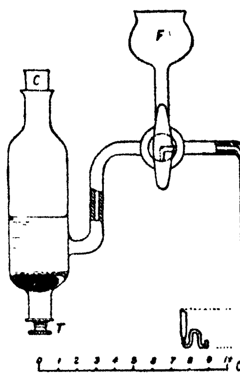

FIG. 34.

The Auxiliary Electrode.—Any of the well-recognised non-polarisable electrodes may be employed as an auxiliary electrode, but the one usually utilised is the $2\,N$ H_2SO_4 electrode. Fig. 34 shows a suitable form of vessel.[1]

To fit this up as a $2\,N$ H_2SO_4 electrode a small amount of mercury is first introduced into the vessel. On to this is poured a paste made by triturating a few drops of mercury with mercurous sulphate and twice normal sulphuric acid until the

[1] H. J. S. Sand, *Trans. Faraday Soc.*, 1909, 5, 160.

whole presents a uniform greyish appearance. Above this is poured some twice normal sulphuric acid, preferably previously saturated with mercurous sulphate by shaking with the latter salt. The tube which contains the liquid forming the electrical connection between the auxiliary electrode and the electrolyte undergoing electrolysis in the beaker is next filled. This tube consists of a capillary of about 2 mm. bore of the form illustrated which can be filled from the funnel F through a two-way tap. The grease from the latter is completely removed by means of ether. When in use, the tap is kept closed, but the film of electrolyte which forms round the barrel owing to the absence of grease furnishes sufficient electrical connection between the two arms of the capillary. The arm adjacent to the auxiliary electrode proper is filled, preferably through the funnel, with twice normal sulphuric acid, whereas the other arm may, if required, contain some other electrolyte such as sodium sulphate. This arm is bent at its end several times at right angles to the plane of the paper in the manner shown in the illustration.

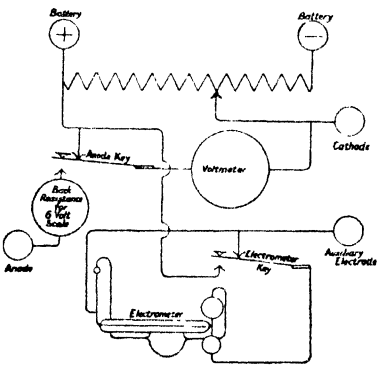

FIG. 85.

Towards the end of an experiment any small amount of liquid from the beaker that may have diffused into the bend is run out by opening the tap leading to the funnel F, for an instant. For measuring the potential between the auxiliary electrode and the cathode, a method must be adopted which absorbs no appreciable current and at the same time is as direct and rapid as possible. It should be accurate to about one centivolt. Fig. 35 shows a suitable arrangement.

The terminals of a dry cell are connected to the two ends of a sliding resistance indicated as battery + and −. Thus any voltage between zero and that of the cell may be tapped off between the slider and one of the ends. The former is moved until this variable voltage just balances the voltage to be measured between the two terminals indicated in Fig. 35 as Cathode and Auxiliary Electrode. The balance is detected by a suitable zero-instrument such as a capillary electrometer. The value of the voltage is then read off directly on a voltmeter placed in parallel.

Fig. 36 represents a box which contains all the instruments mentioned, permanently connected, and provides in addition a connection by means of which the voltage between anode and cathode can be read off directly on a second scale of the voltmeter on

depressing a key marked anode.[1] This connection is also shown in Fig. 35.

An arrangement serving a similar purpose in which the zero-instrument is a galvanometer has been described by A. Fischer.[2]

FIG. 36.

4. Electrodes.

Electrodes of a large variety of forms have been employed for purposes of analysis. The material used in their construction is usually either pure platinum or its alloy with about 10 per cent. of iridium. Owing to the very high cost of these metals numerous attempts have been made to replace them by cheaper materials. As regards the anode, it is improbable that a satisfactory substitute for platinum metals will be found, although the weight of these may be very materially reduced by making the framework of the electrode of glass and confining the precious metal to the working parts.

A suggestion by O. Brunck to replace the platinum by tantalum which has been plated with platinum deserves attention.[3] Tantalum itself when used as an anode does not dissolve in the electrolytes commonly employed in analysis, and this is obviously a condition that even a plated metal must conform to. It, however, becomes covered with a non-conducting film of oxide when not plated with platinum. According to O. Brunck, tantalum can easily be coated with platinum electrolytically, and is also manufactured as wire,

[1] H. J. S. Sand, *loc. cit.*, p. 162.
[2] *Elektro-analytische Schnellmethoden*, p. 100; *Chem. Zeit.*, 1909, 33, 337.
[3] *Chem. Zeit.*, 1912, 36, 1233.

plated by a special process by Siemens and Halske. It is not impossible that tungsten may lend itself to similar application.

For cathodes, metals baser than platinum have been frequently employed. The general rule should be adhered to, that the metal of the cathode be more electro-negative than the metal to be deposited, although cathodes of nickel, a metal which easily becomes passive, have been used for approximate copper determinations.

According to Brunck,[1] tantalum may be employed in the same way as platinum for cathodes in all cases. However, the fact must not be forgotten that electrolytic hydrogen combines with it and renders it brittle. For zinc determinations nickel gauze may be used which may be freed from deposited metal after a determination by means of warm dilute hydrochloric acid. Brass gauze has been

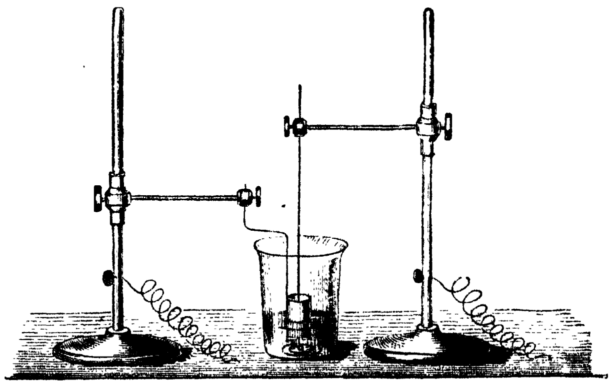

FIG. 37.

similarly employed and electrodes of tin and of copper have also been used.

For copper determinations cathodes of silver have been successfully employed.[2] The deposited metal may be removed from these by means of hot dilute sulphuric acid (1 : 10) to which some hydrogen peroxide, free from hydrochloric acid ($2\frac{1}{2}$ c.c. perhydrol per 100 c.c.), has been added,[3] or by a cold solution containing 20 g. trichloracetic acid, 100 c.c. of ammonia (sp. gr. 0·900) and 100 c.c. of water.[4] If the electrode appears black through roughening after use, it may be brought back to its original condition by ignition.

Mercury is frequently employed as a cathode, and as its application

[1] *Loc. cit.*

[2] *Cf.* H. E. Medway, *Amer. J. Sci.*, 1904, iv., **18**, 180. H. J. S. Sand and W. M. Smalley, *Trans. Faraday Soc.*, 1910, **6**, 205.

[3] H. J. S. Sand and W. M. Smalley, *loc. cit.*

[4] H. W. Doughty and B. Freeman, *J. Amer. Chem. Soc.*, 1921, **43**, 700.

has extended the range of electrical methods in chemical analysis, it will be referred to again below (pp. 101-102).

In the design of electrodes, whether mechanical stirring is resorted to or not, the most important consideration is that they should promote circulation of the liquid. Low resistance of the liquid traversed by the current and good distribution of the latter over the surface of the electrode are also points to which attention should be directed. A considerable advance in the construction of electrodes was made by the introduction of metal gauze.[1]

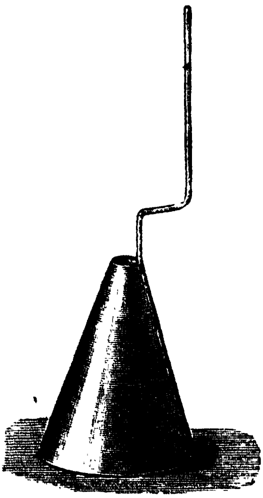

FIG. 88.

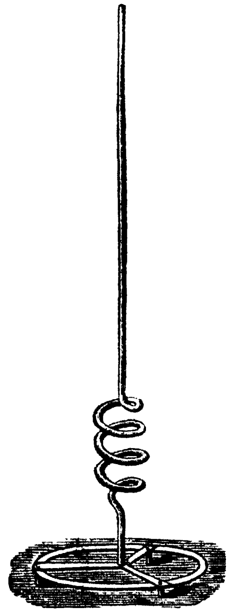

FIG. 89.

Stationary Electrodes.—The following are a few representative types of stationary electrodes.

The electrodes originally employed by Luckow, one of the pioneers of electro-analytical work, are shown in Fig. 37. The cathode is a cylindrical piece of foil, whereas the anode is constructed of wire in such a way that the gas bubbles liberated from it at the bottom of the beaker stir the whole of the electrolyte.

Figs. 38 and 39 show the electrodes, no doubt developed from these, used by the Mansfeld Smelting Works; it is advantageous to have a few slots in the foil (Fig. 38) to facilitate the circulation of the liquid. Fig. 40 shows the same electrodes held by suitable stands, the rods of which are made of glass.

[1] H. Paweck, *Z. Elektrochem.*, 1898, 5, 221. A. Winkler, *Ber.*, 1899, 32, 2192.

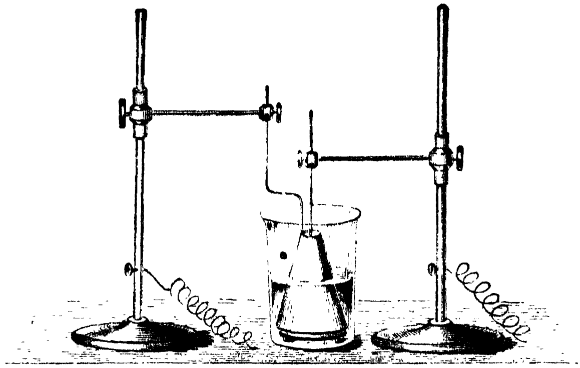

FIG. 40.

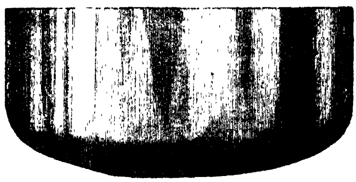

FIG. 41.

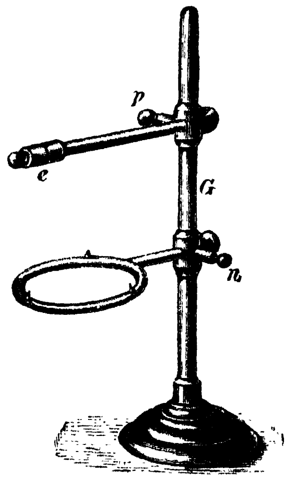

FIG. 42.

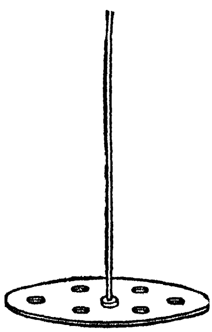

FIG. 43.

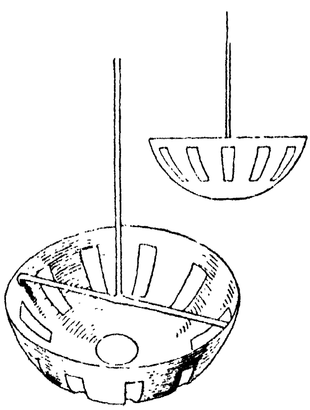

FIG. 44.

Fig. 41 illustrates a platinum dish specially recommended by A. Classen, and Figs. 42, 43, and 44, a stand and anodes that may be used in conjunction with it.

It has frequently been found useful to roughen the working electrode by sand-blasting in order to increase the adherence of the deposit; but such roughening is believed to promote the occlusion of impurities in the deposit.[1] To meet this objection Classen recommends roughening platinum dishes only very slightly by means of dilute *aqua regia.*

The main objections to the platinum dish are the very large amount of platinum required and the poor circulation of the electrolyte. The latter objection can be very largely met by heating the dish gently during electrolysis. For this purpose a circular piece of sheet asbestos

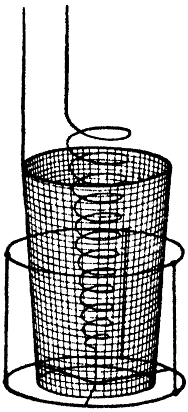

Fig. 45.

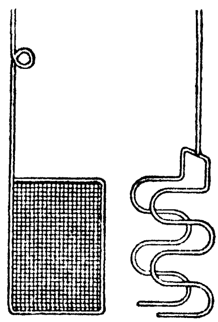

Fig. 46

may be attached to the lower side of the ring supporting the dish and a bunsen burner be placed underneath it. Rapid rotation of the anode by mechanical means has also been extensively applied.

Figs. 45 and 46 illustrate wire gauze electrodes. The former pair, which is due to A. Hollard,[2] may be considered to be a development of the Luckow pattern, the foil of the cathode being replaced by gauze. The latter form is due to F. M. Perkin.[3] Both electrodes may also be constructed of gauze.

When mercury is to be used as a cathode the arrangement shown in Fig. 47, which was elaborated by W. M. Howard[4] in Edgar F. Smith's laboratory, may be employed.

It consists of a small beaker (50 c.c. capacity), near the bottom of

[1] O. Scheen, *Z. Elektrochem.*, 1908, 14, 257.
[2] A. Hollard et L. Bertiaux, *Analyse par Electrolyse*, 1906, p. 11.
[3] F. Mollwo Perkin, *Practical Methods of Electro-Chemistry*, 1905, p. 79.
[4] E. F. Smith, *Electro-Analysis*, 1918, p. 66.

which there is introduced through the side a thin platinum wire. Internally the latter dips into the mercury, while externally it touches a disc of metal on which the beaker rests and by means of which electrical connection to the source of current is made. The anode may be constructed of gauze, or one of the forms depicted in Figs. 39, 43, or 44 may be employed. In the figure the anode is arranged for rotation, but the apparatus may also be employed for stationary electrolytes.

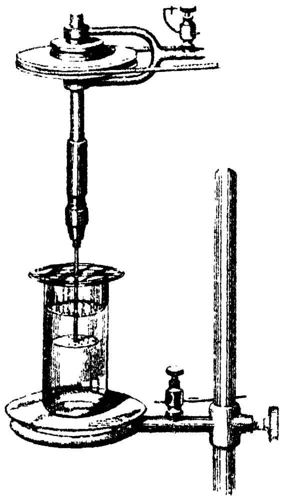

FIG. 47.

Rotating Electrodes.—A very great advance in electrolytic analysis was made by the introduction of vigorous stirring of the electrolyte. Since the metal-ions liberated at a cathode are supplied solely by the layer of liquid in immediate contact with it, their renewal is entirely dependent upon the slow process of diffusion unless convection currents supervene. Thus in 1901 it was shown mathematically by H. J. S. Sand[1] that the film of electrolyte adjoining the electrode may frequently become completely exhausted of metal salt with very great rapidity when high current densities are employed, while the bulk of the liquid still contains large quantities in solution, and that the only way to prevent this is to employ rapid stirring, which thus may alter the whole course of an electrolytic process. It was proved, for example, for an acid solution of copper sulphate, that in one instance in which 60 per cent. of the current was employed in the evolution of hydrogen, vigorous stirring under otherwise identical conditions caused the whole of the current to be utilised in the deposition of copper.

When it is remembered that the success of electrolytic metal-deposition frequently depends on confining the action of the current to only one process, and that the liberation of hydrogen is frequently accompanied by the production of spongy deposits, it will be seen that high current densities may be usefully employed to shorten the duration of the process only when the electrolyte is vigorously stirred. In many cases determinations which require hours in stationary electrolytes may be performed in as many minutes when vigorous stirring accompanied by high current densities is resorted to.

Mechanical stirring applied to electrolytic analysis appears to have been first suggested in 1886 by von Klobukow,[2] and was utilised by various experimenters. Important extensions of this method

[1] *Phil. Mag.*, 1901 [vi.], 1, 45. [2] *J. prakt. Chem.*, 1886, 33, 473.

were published by F. A. Gooch and H. E. Medway[1] in 1903, who rotated a cathode consisting of a platinum crucible of about 20 c.c. capacity at 600 to 800 revolutions per minute, and at the same time employed considerably higher current densities than had been previously utilised. The experimental arrangement was simple. The crucible was driven directly by a small electric motor placed above it with its shaft vertical. An extension of the latter was fitted to a rubber stopper bored centrally, over which the crucible was pressed, and the electrical connection with the battery was obtained through the framework of the motor by means of the spindle and a strip of platinum foil. The anode was a cylindrical piece of platinum.

The method was subsequently extended by F. F. Exner,[2] R. Amberg,[3] and by A. Fischer and R. J. Boddaert,[4] who employed stationary basins as cathodes, and rotated the anodes of one of the forms shown in Fig. 43 or 44, at 600 to 700 revolutions per minute.

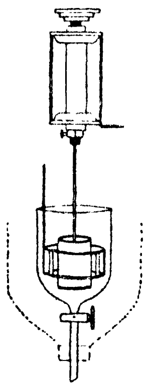

FIG. 48.

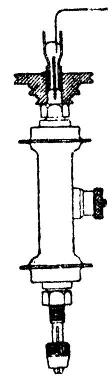

FIG. 49.

A considerable number of other devices for rapid electrolytic analysis have been designed by various investigators, of which the following are typical.

Fig. 48 depicts the electrodes proposed by F. M. Perkin,[5] who, like Gooch and Medway, rotates the cathode. The latter is made of gauze, the anode is constructed of wire and has four baffle plates to minimise the rotation of the liquid as a whole. Attention may be drawn to the use of a bicycle hub to provide a comparatively inexpensive and mechanically very perfect mounting for the rotating spindle. This arrangement, which was first employed at Heathcote's suggestion by T. S. Price and G. H. B. Judge,[6] is lubricated by a mixture of graphite and oil. An appreciable electrical resistance is always present in bearings of this kind, and if it is desired to avoid this, connection can be made through a small cup containing mercury cemented to the top of the spindle, into which the leading-in wire dips (Fig. 49).[7]

The cathode may be attached to the spindle by means of a small chuck. The illustration also shows a vessel for the electrolyte first suggested by Price and Judge,[8] and favoured by many workers, which consists of a tap-funnel from which the electrolyte may be readily withdrawn after a determination.

[1] *Amer. J. Sci.*, 1903, iv., **15**, 320.
[2] *J. Amer. Chem. Soc.*, 1903, **25**, 904.
[3] *Z. Elektrochem.*, 1904, **10**, 386.
[4] *Ibid.*, p. 945.
[5] *Practical Methods of Electrochemistry*, p. 81.
[6] *Trans. Faraday Soc.*, 1906, **2**, 87.
[7] T. S. Price and T. C. Humphreys, *J. Soc. Chem. Ind.*, 1909, **28**, 119.
[8] *Trans. Faraday Soc.*, 1906, **2**, 87.

Electrodes suitable for Use with an Auxiliary Electrode.—The following apparatus was designed by H. J. S. Sand[1] primarily to allow the use of an auxiliary electrode, but it embodies also other features that make it particularly adaptable to varying conditions of electrolytic analysis. The two electrodes are shown in Fig. 50.

They are both constructed of gauze, and when placed in position,

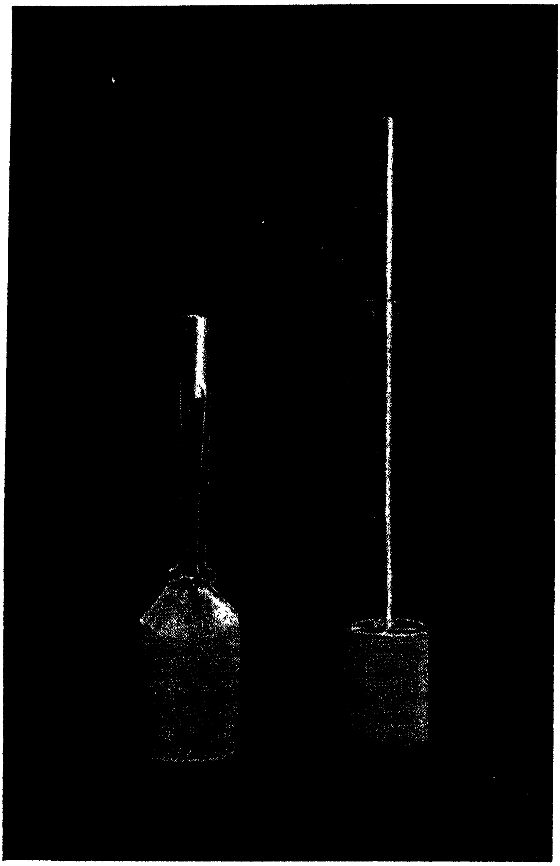

FIG. 50.

the outer (cathode) surrounds the inner to such a degree that the lines of flow of the current are contained completely between the two. The tip of the capillary leading to the auxiliary electrode may therefore be placed anywhere in the electrolyte outside the outer electrode. An important feature in the construction of these electrodes is that they are held in position relatively to each other by a glass tube, in which the hollow stem of the inner one rotates freely, so that the clearance

[1] *Trans. Faraday Soc.*, 1909, 5, 159, and *J. Chem. Soc.*, 1907, 91, 373.

between them may amount to only 3-5 mm. without risk of short circuit. The glass tube is pushed through the collar of the outer electrode by which it is held, the collar in its turn is clamped in the electrolytic stand by means of an ordinary V clamp, the cork from the flat side of which has been removed, and preferably replaced by platinum foil soldered to the metal. The inner electrode may be held by a chuck which is in metallic communication with the rotating spindle of the stand by means of a flexible connection. The framework of both electrodes is preferably made of iridio-platinum. The mechanism for rotating the anode may be constructed in a variety of ways, but Fig. 51 shows how it may be made in a quite satisfactory manner from ordinary laboratory stock.

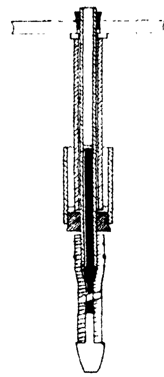

FIG. 51.

The rotating spindle consists of a glass or metal tube of 5 or 6 mm. bore and about 15 cm. length. On one end of this a wooden pulley is clamped by means of a cork, while the other end is continued by a piece of not too thick-walled rubber pressure tubing. Into the latter a chuck is wired by means of an iron peg fitted to it. The whole of the rubber tube and about half of the glass spindle are filled with mercury, and into this dips a short iron wire by means of which the current is led in. A drop of oil may be placed on the top of the mercury. The glass spindle rotates inside a wider metal tube or fairly thick-walled glass tube of about 10 cm. length into which it fits loosely. The top of this tube is ground flat and a metal washer is placed between it and the pulley, the surface of contact being well lubricated with vaseline. The surface of contact between the two glass tubes is kept well oiled. This is achieved by attaching a short piece of wide tube to the bottom of the rotating spindle by means of a well-fitting cork and pouring oil into the trap thus formed to reach above the bottom of the outer tube. This oil is drawn up between the two tubes by capillary action. The whole arrangement is held by a clamp fitted to a heavy stand.

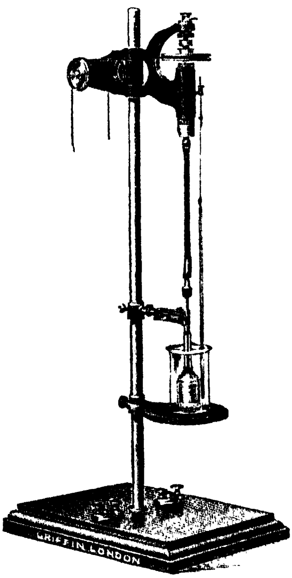

FIG. 52.

Fig. 52 shows an alternative construction on a complete stand. The rotating spindle is here a steel tube mounted in ball bearings.

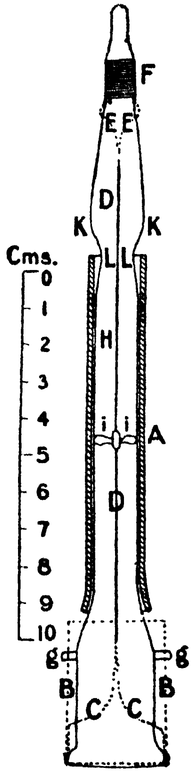

FIG. 53.

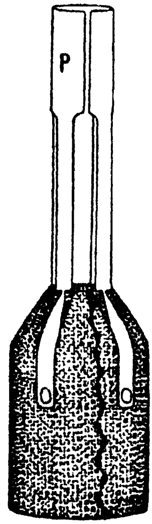

FIG. 54.

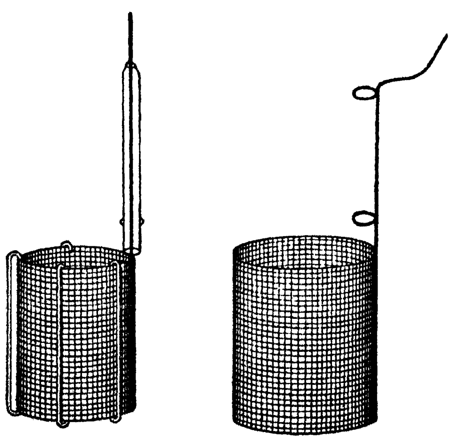

FIG. 55.

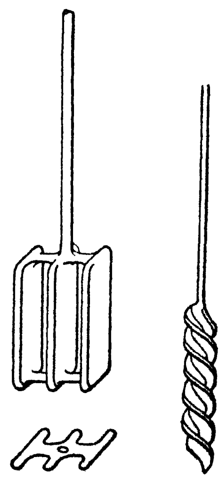

FIG. 56.

Fig. 54 illustrates an outer electrode of essentially the same design as that of Fig. 50, which may be improvised in the laboratory from silver or nickel sheet and gauze. The frame of the inner electrode may also be replaced by one of glass, as shown in Fig. 53.[1]

With the same purposes in view, A. Fischer has suggested two concentric stationary cylinders of wire gauze shown in Fig. 55, and the use of a separate glass stirrer of appropriate shape to stir the liquid, shown in Fig. 56. The electrodes are kept in position relatively to each other at about 3½ mm. apart by three glass rods fastened to the inner electrode and a glass tube surrounding the stem of the latter.

Other Methods of Stirring the Electrolyte.—A number of devices have been proposed to obtain very vigorous circulation of the electrolyte without the use of a motor. An ingenious apparatus of this kind, due to F. C. Frary,[2] is shown in Fig. 57.

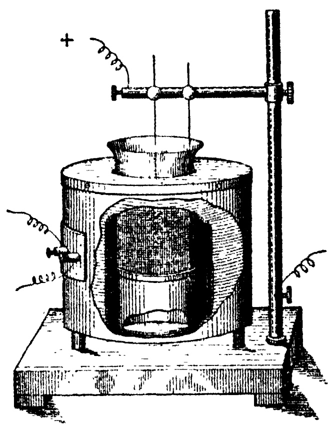

FIG. 57.

As will be seen, the current passes through the electrolyte in the beaker, radially between a central anode and an outer cathode. The beaker is surrounded by a solenoid, the magnetic lines of which intersect the lines of flow of the current at right angles. The result of this is that when a sufficiently large current is employed, rapid rotation of the liquid is produced. Obviously the current cannot be reduced without also diminishing the rotation of the electrolyte, and in other respects too the apparatus will not very readily allow such conditions as temperature and quantity of the electrolyte to be varied.

When simple gauze electrodes and small quantities of electrolyte are employed with very high current density, the vigorous evolution of gas and the heating of the electrolyte may produce so efficient circulation that certain simple determinations may be carried out quite rapidly without mechanical stirring. Thus J. T. Stoddard[3] employed a cylindrical gauze cathode 3 cm. long and 3 cm. in diameter surrounding a cylindrical foil anode 2·5 cm. long and 0·8 cm. in diameter in a small beaker containing altogether about 50 c.c. of liquid, and employed currents varying between 1 and 8 ampères without having recourse to mechanical stirring. About half a gram of metal

[1] H. J. S. Sand and W. M. Smalley, *Trans. Faraday Soc.*, 1910, **6**, 205.
[2] *J. Amer. Chem. Soc.*, 1907, **29**, 1592; *Z. Elektrochem.*, 1907, **13**, 308.
[3] *J. Amer. Chem. Soc.*, 1909, **31**, 385.

was said to have been deposited quantitatively in times varying from about ten minutes to about half an hour. According to T. S. Price and T. C. Humphreys,[1] however, the results obtained in these times are not quantitative.

Two further methods of stirring the electrolyte without the use of a motor have been put forward by F. Fischer, C. Thiele, and E. Stecher.[2] One consists in stirring the electrolyte by means of hydrogen taken from a cylinder through a reducing valve. In the other the vessel in which the electrolysis is carried out is partially evacuated by connecting it to an ordinary laboratory water-injector air-pump. The effect of this is not only to cause the liquid to boil at a much lower temperature, but also to considerably increase the size of the gas bubbles so that the efficiency of stirring is greatly enhanced.

In the form of apparatus in which hydrogen was the stirring agent a large boiling tube of 30 cm. length and 4·5 cm. bore was employed to hold the electrolyte. It had a few constrictions about 5 cm. from the bottom which served as a support for the wire-gauze cathode. A spiral of wire formed the anode.

The apparatus designed for use with the pump was similar to the one just described, but here the gauze cathode was placed at the bottom of the boiling tube. Although the results obtained with this form of apparatus prove that it is quite possible to obtain vigorous circulation of the electrolyte without making use of a motor, yet the general adaptability of such arrangements is not very high, and they fail particularly where any extension of existing methods is sought.

The Use of Mercury Cathodes.

The precipitation of metals into mercury with stirring has been referred to above (p. 101). By an arrangement of the kind shown in Fig. 47, all troubles arising from the deposition of the metal in a loose and spongy form are avoided. On the other hand, a small loss of mercury owing to evaporation is apt to occur. This danger is minimised by washing with alcohol and ether and drying at ordinary temperature. Great attention must be paid to keeping the inside of the cell absolutely clean, or drops of the amalgam cling to the glass and may possibly be lost. Many of the advantages of mercury electrodes may be obtained with other metals if these are coated with a layer of mercury by electro-deposition before use.

The use of mercury cathodes has, in the hands of Edgar F. Smith and his collaborators, considerably extended electrical methods of chemical analysis. Thus if a neutral solution of copper or zinc sulphate be electrolysed with a mercury cathode and platinum anode, the

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 307. [2] *Z. Elektrochem.*, 1911, **17**, 905 and 906.

sulphuric acid is quantitatively liberated and may be determined by direct titration. If the anode be plated with silver, then chlorides, bromides, and salts generally, the anions of which form insoluble silver salts, may be quantitatively analysed; the anion combining with the silver may be weighed on the anode, the cathion at the same time being deposited into the mercury. The latter precipitation takes place even when the cathion is an alkali, or alkaline-earth ion, though, insoluble or sparingly soluble hydroxides may then be formed which tend to separate out in the liquid adjoining the cathode.

These facts have been utilised by J. H. Hildebrand[1] in the design of a cell in which anions forming insoluble silver salts and cathions such as sodium that form soluble hydroxides may be determined simultaneously. In principle it resembles the Castner-Kellner cell for the manufacture of caustic soda. It is illustrated in Fig. 58.

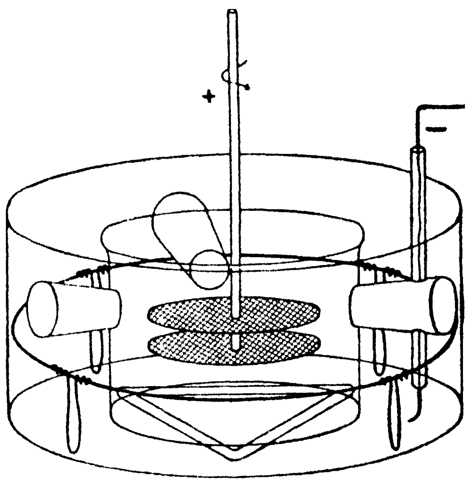

FIG. 58.

The apparatus comprises an outer cell consisting of a crystallising dish 11 cm. in diameter and 5 cm. deep. Inside this is a beaker 6 cm. in diameter, the bottom of which has been cut off so that a ring is formed 4·5 cm. high. This rests on a large triangle of thin glass rod on the bottom of the crystallising dish, and is kept in position by three rubber stoppers as shown. The object of this ring is to allow the inner compartment to be hermetically sealed from the outer by means of mercury. A film of solution, however, was found to form between the glass and the mercury, permitting a small quantity of salt to diffuse from the inner to the outer compartment. To prevent this the lower rim of the bottomless beaker was first platinised and then silver-plated to a width of about 4 mm. This was effected by use of a saturated solution of chloroplatinic acid, to which an equal volume of glycerin was added; this solution was painted on, the beaker dried at 300°, and afterwards carefully heated in a Bunsen flame till the glass just began to soften. The film of adherent platinum was then made the cathode in an agitated solution of potassium silver cyanide, and a heavy layer of silver deposited on it which was finally amalgamated by agitating it with mercury.

[1] *J. Amer. Chem. Soc.*, 1907, 29, 447.

In the outer compartment there is a ring of about six turns of nickel wire, supported about 1 cm. above the surface of the mercury by wire legs.

In using this cell, which must be kept scrupulously clean, pure mercury is poured in so that its level is about 3 mm. above the lower edge of the bottomless beaker. The anode should be fitted about 5 mm. above the surface of the mercury and be rotated at about 300 revolutions per minute. The current is led out of the cell directly from the mercury. The solution to be electrolysed is put into the inner compartment; sufficient distilled water to cover the nickel wire is placed in the outer compartment, and to this is added 1 c.c. of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is decomposed as soon as it comes into the outer division, the latter acting as a galvanic cell, the plates of which are sodium-amalgam and nickel respectively, and the electrolyte, sodium chloride. The sodium hydroxide formed in the outer compartment is determined directly by titration.

5. General Remarks; Disconnecting and Drying the Electrodes.

In electrolytic analysis, the apparatus should always be kept scrupulously free from grease, and the working parts should never be touched with the fingers. This is especially essential when good deposits are to be obtained from the smaller current densities employed with stationary electrodes. The bulk of the liquid should be kept as small as the electrodes employed will allow, so as to facilitate circulation, for it is easier to stir a small volume, but even with equally efficient circulation for all volumes, the time required for a deposition will be approximately proportional to the bulk of the liquid. A certain amount of spraying is always likely to occur during electrolysis. The beaker or other vessel is therefore usually covered with split clock glasses which have been suitably notched to admit the electrodes. Slips of mica, which are easy to cut and less liable to be broken, may also be employed. Towards the end of a determination the cover glasses may be washed down, although as a rule sufficient washing is effected by the water formed by condensation from vapours arising from the liquid.

Before disconnecting the electrodes after the precipitation of a metal, its complete absence from the electrolyte should, wherever possible, be tested for chemically. Where this is not possible, a plan frequently adopted with stationary electrodes, is to increase the volume of the electrolyte slightly by the addition of a little water, and to make certain that no further deposit appears after some time on the part of the electrode thus freshly covered by the electrolyte.

When the potential of the electrode is kept under control in rapid electrolytic analysis, the ammeter in very many cases offers sufficient indication of the removal of the metal to be determined. The current is usually started at about 3 to 4 ampères; the cathode potential is then determined and kept constant. Since the action of the current is, as a rule, confined to only one electro-chemical process, the current goes down to a small residual value of say 0·2 or 0·3 ampères when the greater part of the metal has disappeared from solution. After this, the potential of the cathode is gradually raised by altogether about 0·2 volt, until the current which at first rises has gone down to a constant value again, at which it is kept for about two or three minutes. To obtain an insight into the theory of this method of working, it must be remembered that raising the potential of the cathode by about 7 centivolts at a temperature of about 80° or 90° corresponds, after equilibrium has been reached, to a reduction of the metal, if univalent, to one-tenth of its former concentration in the solution; raising the potential by twice this value to the reduction of the metal to one-hundredth of its original concentration, etc.

If the metal ion be bivalent, only half of the increase of potential, *i.e.* about 0·035 volt, is necessary to effect the same ratio in reduction of concentration; if the ion be tervalent, one-third of the difference of voltage will have the same effect. Unfortunately this extremely convenient method of following the progress of a determination can only be employed when no substances are present, such as nitric acid and oxides of nitrogen, which are slowly reduced at the cathode, or such substances as iron salts, which produce a large residual current by alternate oxidation and reduction at the two electrodes. The residual current may be very much diminished by adding powerful reducing substances, such as hydrazine sulphate or hydroxylamine hydrochloride to the electrolyte.

In most acid solutions, the metal dissolves when the current is interrupted after deposition, and therefore the electrical connections should be left intact while the electrolyte is being displaced by water. This is frequently done by introducing a syphon tube filled with water into the beaker or dish so that the electrolyte may be slowly run off from the bottom while it is being replaced by pouring in pure water.

With the arrangement depicted in Fig. 42, the electrodes may be bodily transferred by means of the stand into a beaker filled with pure water and then disconnected. In a similar manner, if the electrodes are held sufficiently rigidly by the stand and the beaker was originally placed on a tripod or some blocks of wood, it may be removed from under the electrodes and rapidly replaced by another one filled with water.

When the liquid is mechanically stirred, the funnel shown in Fig. 48

may be employed and the electrolyte withdrawn at the end of the experiment by means of the tap, while pure water is slowly poured in at the top.

After their removal from the wash-water, the electrodes are usually washed with alcohol and ether, special wash-bottles being used for this purpose, and then dried either in an oven or by holding over a flame.

A very simple method of washing requiring less wash-water than the other methods described may be employed in conjunction with a stand and electrodes of the type used by the present writer (pp. 104-106). With these electrodes a few drops of distilled water should be poured into the glass tubes in which the anode rotates a few minutes before the end of a determination in order to displace any solution that may have been trapped in the tube. The clock-glasses are then removed, and the tripod or ring, on which the beaker stands, is removed from under it. A wash-bottle with water is then taken in the right hand and the beaker slowly lowered while the electrodes are being washed, with the stirrer still running. As soon as the liquid has been lowered completely away from the electrodes, the motor is stopped. For this purpose a switch or disconnecting gear should be placed conveniently on the stand. The beaker with the electrolyte is then replaced by an empty one, the tripod or ring being returned to its original position and the electrodes disconnected. The pair may be conveniently removed simultaneously by holding only the stem of the inner electrode. The cathode is finally dipped successively into a jar containing alcohol, and another containing ether, and dried by holding over a Bunsen burner for a few minutes.

III.—SOLUTIONS EMPLOYED FOR ELECTROLYTIC ANALYSIS

1. Composition of the Solution.

An essential condition in regard to the composition of the solution is that it should conduct the current well. For this reason the presence of salts which conduct the current without taking part in the processes occurring at the electrodes is beneficial. Such "conductivity salts" arising from the neutralisation of acids and alkalis are often present as a result of preliminary chemical operations performed on the electrolyte. Another point of importance is, that the electrolyte should not change in character while the metal is being deposited. For this reason neutral solutions from which deposits of hydroxide are liable to form are, as a rule, avoided and simple acid solutions taken whenever possible. Chlorides are seldom employed, sulphates and nitrates being

usually preferred. One of the reasons for this is that there is sometimes a tendency for the deposited metal to take up small quantities of chlorine from the electrolyte; the principal reason, however, is that chlorine may be liberated at the anode and attack it. This may be avoided by the addition of suitable powerful reducing agents. Thus Engels[1] in 1896 deposited tin from solutions containing small amounts of chlorides to which he added hydroxylamine sulphate, later Sand[2] deposited the same metal from solutions containing considerable quantities of free hydrochloric acid after adding hydroxylamine hydrochloride, and recently E. P. Schoch and D. J. Brown[3] have extensively employed chlorides in the presence of hydroxylamine hydrochloride for the separation of metals.

Very frequently complex compounds of the metal to be deposited, usually in feebly alkaline solution, are employed. The reason for this is a two-fold one. First, some metals show a tendency to deposit in loose crystals from simple electrolytes, whereas they form dense adherent deposits if complex electrolytes are used. The very general rule holds that the more complex the solution of a given metal, *i.e.*, the higher the deposition-potential, the more fine-grained is the metal. The second reason why complex electrolytes are employed is that their application very greatly extends the range of electrolytic metal separations. Thus, for example, in nitric acid solution of copper and bismuth salts, the deposition-potential of bismuth follows so closely on that of copper that a quantitative separation of the two metals is not possible. In a hot solution, however, containing free tartaric acid, the bismuth forms complex compounds to a very much greater extent than the copper, so that if the amount of bismuth present is small, a quantitative separation may be effected. If, on the other hand, this solution be made alkaline and potassium cyanide added, the copper forms complex cyanides to a preponderating extent, and as a result the bismuth can then be quantitatively separated at suitable potentials before the copper begins to deposit. In a similar manner copper is deposited very much before cadmium in acid solution; if, however, the solution be made alkaline, and potassium cyanide added, the formation of complex cyanides is so much greater in the case of the former metal than in that of the latter that cadmium may be separated at potentials at which copper does not begin to deposit. While the value of solutions of complex salts is thus apparent, the fact must not be lost sight of that the deposits obtained from them show a distinct tendency to give high results owing to the inclusion of non-metallic impurities. In most cases this is probably due to the formation of colloidal substances in solution.

[1] *Z. Elektrochem.*, 1896, **2**, 418.
[2] *J. Chem. Soc.*, 1908, **93**, 1577.
[3] *J. Amer. Chem. Soc.*, 1916, **38**, 1660.

2. Influence of Temperature.

Since an increase of temperature causes as a rule a decrease of transfer resistance and of metal over-voltage, the separation of one metal from another may be performed with greater precision and ease at a high than at a low temperature. Although the fact appears to be established that metal deposits formed at a high temperature are more coarse-grained than those produced at a low one, yet most analysts will agree that the adherence of a deposit on a platinum electrode is usually improved by raising the temperature. Another advantage gained by the employment of a high temperature is the very considerable decrease in the resistance of the electrolyte.

3. Influence of Concentration.

The effect of concentration of the metal-ion to be deposited on the nature of the deposit is probably small in all cases in which complete exhaustion in the film adjoining the electrode is guarded against by maintaining the stirring efficiency sufficiently high and the current sufficiently low.

IV.—GENERAL PRINCIPLES UNDERLYING THE SEPARATION OF METALS FROM EACH OTHER

The fact that certain metals are deposited quantitatively as peroxides on the anode has already been referred to and may be utilised to separate them from others. Thus, if a solution of lead nitrate be acidified sufficiently with nitric acid to make the precipitation of metallic lead on the cathode impossible, the lead may be quantitatively precipitated as the peroxide (PbO_2) on the anode and thus completely separated from such metals as copper, cadmium, or zinc. In a similar manner manganese may, by the use of suitable electrolytes, be separated from other metals as hydrated manganese peroxide.

The general principle underlying the electrolytic separation of metals from each other as such is the utilisation of differences of deposition-potential (see pp. 95, 105). The fact that the method can be very greatly extended by the use of complex salts has already been referred to. Where the difference in deposition-potential of the metals to be separated is considerable, *e.g.*, of copper and cadmium, the control of the potential difference between cathode and anode may often be found sufficient. It is, however, very often possible to bring about conditions under which the more electro-positive metal cannot be precipitated with moderate current densities. This can be done by

making the solution fairly acid and working at a high temperature. Hydrogen will then be liberated in preference to the more electro-positive metal. If an oxidising acid such as nitric acid is added, this will further hinder the liberation of the more electro-positive ion, since its reduction will, as a rule, begin at even lower potentials than the liberation of hydrogen.

The most electro-positive metal that can be precipitated quantitatively from aqueous solution on solid cathodes is probably zinc, and to effect this, both the temperature and the hydrogen-ion concentration must be low, *i.e.*, only a feeble acid such as acetic must be present in small concentration. Oxidising substances such as nitrates must be absent.

The still more electro-positive metals, aluminium, the alkaline earths and the alkali metals cannot be precipitated by electrolysis from aqueous solution on solid cathodes under ordinary conditions, and therefore all metals capable of deposition on solid cathodes may be readily separated from these.

Many metal ions capable of liberation from the simpler solutions become incapable of deposition by converting them into complex anions. Thus tin is incapable of precipitation from a cold strongly alkaline solution of sodium thiostannate in which a large amount of sodium sulphide is present. Antimony may be precipitated from a similar solution of sodium thio-antimonate, and on this fact a method for the separation of the two metals is based.

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PHYSICAL MEASUREMENTS EMPLOYED IN TECHNICAL ANALYSIS

By J. S. G. THOMAS, D.Sc., Physicist to the South Metropolitan Gas Company, London

INTRODUCTION

THE aim of this section is to describe the more important methods employed in chemical technology for the measurement of certain physical properties which are of value in technical analysis. From the nature of these measurements it is customary to regard them as physical rather than as chemical, although it is not suggested that any marked dividing line separates the realm of physical measurement from that of chemistry.

At the basis of the science of physical measurement is the fact that the measure of almost all physical quantities can be expressed in terms of three fundamental entities—those of mass, length, and time. The most generally accepted unit of length is the centimetre, the unit of mass the gram, and the unit of time the second. These are the fundamental units of the c.g.s. system. The conversion of the magnitude of any quantity expressed in one system of units to any other system of rational units, is an easy matter when the relation of the fundamental units in the two systems, to one another, is known. Thus, by way of illustration, the conversion of the number expressing the number of grams per cubic metre to pounds per cubic foot requires a knowledge of the relation of the gram to the pound, and of the centimetre to the foot. The necessity for the conversion of any physical quantity from one set of units to another set of units frequently arises in technical chemistry; suitable tables are available for this purpose.

I.—DETERMINATION OF SPECIFIC GRAVITY

The term "specific gravity" means the ratio of the true weight of a given volume of a substance to the true weight of an equal volume of water at the same temperature,—indicated as $d\frac{t}{t}$. Specific gravity being therefore the ratio of two weights, is a number independent

of the fundamental units of the system employed. In this respect, specific gravity is contrasted with density, the latter being defined, in the case of solids and liquids more especially, as the mass per unit volume of the substance. Consequently, the value of the density of a substance is dependent upon the units of the system in which the density is expressed. Now the unit of mass is so related to the unit of length in the c.g.s. system, that the volume of 1 gram of water at 4° C.[1] is 1 c.c. (actually experiments have shown that the volume at 4° C. is 1·000027 c.c.).[2] It follows, therefore, that in the c.g.s. system, the numbers expressing the specific gravity and the density are the same. When the weight of a substance is determined in air, a correction for the air displaced by the substance and by the weights employed is practically never made in technical practice, and the specific gravity of the substance is then taken as signifying the ratio of the apparent weights of the substance in air and of an equal volume of water at the same temperature. Should it be necessary to reduce readings to vacuo, this can readily be effected by the use of the table contained in *Physical and Chemical Tables*, by Kaye and Laby, 4th ed., 1921, p. 21.

Instead of being expressed in terms of the weight of an equal volume of water at the same temperature, the specific gravity of a substance is often expressed in terms of the weight of an equal volume of water at 4° C., and indicated by $d\frac{t}{4}$. The relation between the two quantities is easily seen to be—

$$d\frac{t}{4} = d\frac{t}{t} \times \text{density of water at } t^\circ.$$

The following table gives the density of water over the range from 0° to 39°, at intervals of 1°. More complete tables will be found in *Récueil de Constantes Physiques*, *Société Française de Physique*, 1913, pp. 134-138.

Table of the Density of Water.

Temp.	Density.	Temp.	Density.	Temp.	Density.	Temp.	Density.
0°	0·9998676	10°	0·9997271	20°	0·9982303	30°	0·9956732
1	0·9999266	11	0·9996324	21	0·9980186	31	0 9953670
2	0·9[illegible]99680	12	0 9995246	22	0·9977966	32	0·9950522
3	0·9999920	13	0·9994041	23	0·9975645	33	0·9947290
4	1·0000000	14	0·9992713	24	0·9973225	34	0·9943975
5	0·99[illegible]9918	15	0·9991261	25	0·9970708	35	0·9940578
6	0·9999680	16	0·9989697	26	0·9968097	36	0·9937101
7	0·9999293	17	0·9988014	27	0·9966391	37	0·9933545
8	0·9998759	18	0·9986220	28	0·9962594	38	0·9929911
9	0·9998084	19	0·9984315	29	0·9959708	39	0·9926200

[1] Unless otherwise stated, all temperatures refer to the Centigrade scale. [2] Chappuis, 1907.

As unit of volume, Mohr proposed to take the volume of 1 gram of water at 17·5° weighed in air with brass weights. It can readily be deduced that 1 Mohr litre = 1·0023 true litre, measured in terms of water at 4°. The Mohr unit is often employed in volumetric analysis.

In general, in chemical technology, occasions arise necessitating the determination of specific gravity more frequently in the case of liquids than in the case of solids or gases.

A very simple and quick method for the determination of the specific gravity of liquids, consists in weighing the amount of liquid contained in a pipette of 1 c.c. volume, provided with almost capillary tubes. The pipette is graduated to *contain* 1 c.c. of liquid at any desired temperature, and the pipette is filled to the mark with the liquid at the required temperature, and transferred to the balance. In weighing, the pipette is supported on the pan in a horizontal position by means of a bent wire support. According to Ostwald, the method is accurate to 0·001. More exact results are said to be obtained with pipettes surrounded with a Dewar vacuum jacket, but the necessary adjustment and manipulation are then less simple.

HYDROMETERS

Most frequently the specific gravity of a liquid is determined by means of a hydrometer. Hydrometers must not be greasy, soiled, or damp, before introduction into the liquid; they must be immersed carefully, and must be read from below, at the height of the meniscus, that is, at A_1 A_2 and not at B_1 B_2 (Fig. 59).

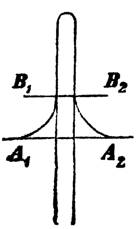


FIG. 59.

Various scales are in use with such hydrometers, and it will perhaps assist in understanding the origin and inter-relation of such scales if some little attention be paid to the theory of the hydrometer. Consider then a hydrometer, the volume of the bulb up to what we may regard as the zero of the stem being V. Suppose the length of stem is divided into n equal parts, each of volume v. Further, let the hydrometer, immersed in a liquid of specific gravity ρ_1, sink to the division n_1 (reckoned from zero) on the stem, and when immersed in a liquid of specific gravity ρ_2, let the corresponding reading be n_2. Let W be the weight of the hydrometer. As a deduction from Archimedes' principle, it follows that the weight of a floating body in a fluid is equal to the weight of fluid displaced.

$$\text{Therefore} \qquad W = (V + n_1 v)\rho_1 \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

$$W = (V + n_2 v)\rho_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

$$\text{From (i.),} \qquad n_1 = \frac{W}{v\rho_1} - \frac{V}{v} \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

$$\text{From (ii.),} \qquad n_2 = \frac{W}{v\rho_2} - \frac{V}{v} \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

$$\therefore \text{ From (iii.) and (iv.)} \quad (n_1 - n_2) = \frac{W}{v}\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right).$$

If, therefore, the stem of the hydrometer (assumed throughout uniform in cross-section) were divided into a number of equal lengths and numbered accordingly, the difference of the readings of the hydrometer in two liquids of different specific gravity would be proportional to the difference of the reciprocals of the respective specific gravities. Hydrometers graduated so as to indicate specific gravity directly are graduated in this manner, and such hydrometers are fairly often used for liquids lighter than water, but practically never in the case of liquids heavier than water. The nearest approach to direct reading is afforded by Twaddell's hydrometer. The graduation in Twaddell's hydrometer is made on the principle just explained, but the divisions on the scale are numbered in degrees, each of which corresponds to a difference of 0·005 in the specific gravity. The zero of the scale corresponds to the point to which the hydrometer sinks in water (generally the water is taken at 15°), so that

$$\text{Specific gravity} = 1 + 0.005\,T,$$

where T is the reading of the hydrometer in degrees Twaddell. Thus, *e.g.*, 8° Tw. = 1·040. No table is therefore required for the conversion of degrees Twaddell into ordinary specific gravity, and the value of the degree Twaddell is quite definite. To cover the range from 1·00 to 1·85 a set of six spindles is employed. It is remarkable that this rational and practical hydrometer should be almost universally used in this country, which is so very conservative and unpractical with regard to weights and measures, whilst the continental nations, which have all adopted the metric system of weights and measures (with the exception of Russia), have not yet adopted a rational hydrometer. In the scale of Fleischer's "densimeter,"[1] which resembles the Twaddell scale, each division represents a change of 0·01 in specific gravity, so that

$$\text{Specific gravity} = 1 + 0.01\,F.,$$

where F. is the reading on the Fleischer scale. The degrees on this scale are rather large, and the scale has fallen into disuse largely owing to that fact, and been displaced by the Twaddell scale, the degrees in the latter being half as large as those in Fleischer's.

The specification of a hydrometer scale in which the degrees are

[1] *Dingl. polyt. J.*, 1876, **222**, 159.

represented by equal lengths of the stem is certainly attractive. For graduation purposes, such a specification offers many advantages over the direct reading variety. In translating the abstract notion of such a scale of degrees into a working instrument, confusion has resulted. Baumé's is the chief hydrometer graduated in divisions of equal lengths, and is in common use in the United States and on the Continent. Baumé's original specification of the scale is as follows:—For liquids denser than water, 15 parts of pure sodium chloride are dissolved in 85 parts of water at a temperature of 10° Réaumur (12·5° C.; 54·5° F.). The zero of the scale is the point to which the hydrometer sinks in distilled water, and the point to which it sinks in the 15 per cent. solution of salt is marked 15. The distance between the zero and this point is divided into 15 equal parts, and the stem graduated with a similar number of equal divisions. For liquids lighter than water the zero is determined by a 10 per cent. solution of sodium chloride, and the division 10 is given by distilled water. The definition of the scale is unsatisfactory in many respects, *e.g.* the salt actually used was seldom pure and dry. Numerous attempts have been made to improve the specification of the Baumé scale, and such attempts have resulted in the production of a large number of confusing scales. C. F. Chandler[1] examined various Baumé scales on the market, and his investigations disclosed thirty-four different Baumé scales, none of which were correct. Gerlach determined the specific gravity of a 10 per cent. salt solution and gave the value 1·07311 at 14° R. (17·5° C.), and from this he calculated a table comparing Baumé degrees with specific gravities.[2] The Gerlach scale is now practically never used; the lower degrees do not agree with those ordinarily used, and the higher ones show extraordinary differences.

The modern practice is to mark the hydrometers 66° B. at the point to which they sink in "English sulphuric acid" (*i.e.*, sulphuric acid of concentration 93 to 95 per cent. H_2SO_4) at 17·5° C., and to divide the space between this and 0° into 66 equal parts by length. Here, again, uncertainty is introduced by the definition "English sulphuric acid." Pure acid was certainly never used, as is proved by the fact that the specific gravity, 1·842, which is usually considered the equivalent of 66° B., is certainly greater than that of pure sulphuric acid at 17·5° C., even at its point of maximum density (97 per cent. H_2SO_4).

The general state of confusion evidenced above, led Kolb, in France, to attempt to construct a "rational" Baumé scale, based upon the following considerations:—

Let W be the weight of the hydrometer, and V the volume up to zero, the reading when the hydrometer is immersed in water ($d=1$). Suppose $n°$ is the reading when the hydrometer is immersed in a liquid

[1] *Acad. Nat. Sciences*, Philadelphia, 1881. [2] *Dingl. polyt. J.*, 1870, **198**, 315.

of density d, and let v be the volume of one degree of the stem, the density of water being 1·000, then

$$W = V = (V - nv)d$$

$$\text{hence} \quad d = \frac{W}{V - nv} = \frac{W}{W - nv}.$$

If the stem be considered as having unit cross-section, so that the volume of stem represented by one degree is unit volume, then $v = 1$, and

$$d = \frac{W}{W - n} \quad \text{or} \quad W = \frac{nd}{d - 1}.$$

Taking the modern practice whereby 66° B. corresponds to specific gravity 1·842 at 15° C., it follows that

$$W = \frac{66 \times 1.842}{0.842} = 144.3(8)$$

$$\text{and} \quad d = \frac{144.3}{144.3 - n}.$$

This is the relation between the specific gravity and the reading "n" on the "rational" Baumé scale. It is not without interest to notice that calculation gives the value of W as more nearly 144·4 than 144·3, although the latter figure is the one accepted. Various other so-called "rational" Baumé scales have been based on a formula similar to the above, differing only in the value of the constant W.

For liquids heavier than water, as already shown, the relation between the Baumé reading and the specific gravity of the liquid is given by a relation of the form—

$$d = \frac{W}{W - n}.$$

A slightly modified relation expresses the relation between the rational Baumé reading and the specific gravity of a liquid lighter than water. These latter are deduced from the corresponding scales for liquids of specific gravity greater than 1, by the substitution of the formula—

$$d = \frac{W}{(W - 10 + n)},$$

the corresponding value of W being used. The following table contains formulæ calculated from the values d for the specific gravity of a 10 per cent. salt solution at the respective temperatures stated:—

Temperature °C.	Specific gravity d.	Liquid heavier than Water.	Liquid lighter than Water.
12·5	1·073596	$d = \frac{145 \cdot 88}{145 \cdot 88 - n}$	$d = \frac{145 \cdot 88}{135 \cdot 88 + n}$
15·0	1·073350	$d = \frac{146 \cdot 3}{146 \cdot 3 - n}$	$d = \frac{146 \cdot 3}{136 \cdot 3 + n}$
17·5	1·073110	$d = \frac{146 \cdot 78}{146 \cdot 78 - n}$	$d = \frac{136 \cdot 78}{136 \cdot 78 + n}$

The relation $d = \frac{146 \cdot 78}{146 \cdot 78 - n}$ is used in connection with solutions of sucrose. In addition to Baumé scales already mentioned, two other Baumé scales for liquids heavier than water are to be mentioned, viz., that used in Holland, in which $d = \frac{144}{144 - n}$, and that used in America, in which $d = \frac{145}{145 - n}$.

The following table gives the relation between the specific gravity and the corresponding Baumé readings on various scales :—

Relation between the Specific Gravity and the corresponding Baumé Readings on various Scales for Sp. Gr. less than 1.

Degrees n.	Specific gravity. "Rational" Baume. $d = \frac{144 \cdot 3}{144 \cdot 3 - n}$	Specific gravity. American Baumé. $d = \frac{145}{145 - n}$	Specific gravity. $d = \frac{146 \cdot 78}{146 \cdot 78 - n}$	Degrees n.	Specific gravity. "Rational" Baumé. $d = \frac{144 \cdot 3}{144 \cdot 3 - n}$	Specific gravity. American Baumé. $d = \frac{145}{145 - n}$	Specific gravity. $d = \frac{146 \cdot 78}{146 \cdot 78 - n}$
1	1·0070	1·0069	1·0069	34	1·3083	1·3063	1·3015
2	1·0141	1·0140	1·0138	35	1·3202	1·3182	1·3131
3	1·0212	1·0211	1·0209	36	1·3324	1·3303	1·3250
4	1·0285	1·0284	1·0280	37	1·3448	1·3426	1·3370
5	1·0359	1·0357	1·0353	38	1·3575	1·3551	1·3493
6	1·0434	1·0432	1·0426	39	1·3704	1·3679	1·3618
7	1·0510	1·0507	1·0501	40	1·3835	1·3810	1·3746
8	1·0587	1·0584	1·0576	41	1·3969	1·3942	1·3876
9	1·0665	1·0662	1·0653	42	1·4106	1·4078	1·4008
10	1·0745	1·0741	1·0731	43	1·4245	1·4216	1·4143
11	1·0825	1·0821	1·0810	44	1·4387	1·4356	1·4281
12	1·0907	1·0902	1·0890	45	1·4532	1·4500	1·4421
13	1·0990	1·0985	1·0972	46	1·4680	1·4646	1·4564
14	1·1074	1·1069	1·1054	47	1·4830	1·4796	1·4710
15	1·1160	1·1154	1·1138	48	1·4984	1·4948	1·4860
16	1·1247	1·1240	1·1223	49	1·5142	1·5104	1·5011
17	1·1335	1·1328	1·1310	50	1·5302	1·5263	1·5166
18	1·1425	1·1417	1·1398	51	1·5466	1·5426	1·5325
19	1·1516	1·1508	1·1487	52	1·5634	1·5591	1·5486
20	1·1609	1·1600	1·1578	53	1·5805	1·5761	1·5652
21	1·1703	1·1694	1·1670	54	1·5980	1·5934	1·5820
22	1·1799	1·1789	1·1763	55	1·6159	1·6111	1·5993
23	1·1896	1·1885	1·1858	56	1·6342	1·6292	1·6169
24	1·1995	1·1983	1·1955	57	1·6529	1·6477	1·6349
25	1·2096	1·2083	1·2053	58	1·6721	1·6667	1·6533
26	1·2198	1·2185	1·2153	59	1·6917	1·6860	1·6721
27	1·2302	1·2288	1·2254	60	1·7117	1·7059	1·6914
28	1·2407	1·2393	1·2357	61	1·7323	1·7262	1·7111
29	1·2515	1·2500	1·2462	62	1·7533	1·7470	1·7313
30	1·2625	1·2609	1·2569	63	1·7749	1·7683	1·7520
31	1·2736	1·2719	1·2677	64	1·7970	1·7901	1·7732
32	1·2849	1·2832	1·2788	65	1·8197	1·8125	1·7948
33	1·2965	1·2946	1·2900	66	1·8429	1·8354	1·8170

In the case of liquids lighter than water, again various scales are in use. The Baumé hydrometer for liquids lighter than water is graduated in one or other of two ways, the specific gravity corre-

sponding to any reading n° being given either by the relation, $d = \frac{146}{136+n}$, or by the American formula, $d = \frac{140}{130+n}$.[1] Cartier's hydrometer is graduated so that 21^c corresponds with 21° B. on the instrument for liquids lighter than water; above and below this point 16° B. = 15° Cartier. The Cartier degrees are therefore larger than the Baumé degrees in the ratio 16 : 15. Beck's hydrometer is graduated so that the zero corresponds with $d = 1{\cdot}000$ and 30° represents a density 0·850; one-thirtieth of the intermediate distance is taken as 1° and graduations of the value are made both above and below the zero.

The following table gives the relation between the degrees on the various scales and the specific gravity :—

Relation between the degrees on various Hydrometer Scales and the Specific Gravity for Sp. Gr. less than 1.

Degrees Baumé. American Baumé. Cartier or Beck.	Baumé. $d=\frac{146}{136+n}$ Sp. gr.	American Baumé. $d=\frac{140}{130+n}$ Sp. gr.	Cartier. Sp. gr.	Beck. Sp. gr.	Degrees Baumé. American Baumé. Cartier or Beck.	Baumé. $d=\frac{146}{136+n}$ Sp. gr.	American Baumé. $d=\frac{140}{130+n}$ Sp. gr.	Cartier. Sp. gr.	Beck. Sp. gr.
0	...	...	...	1·0000	36	0·8488	0·8434	0·8439	0·8252
1	...	...	...	0·9941	37	0·8439	0·8383	0·8387	0·8212
2	...	...	...	0·9883	38	0·8391	0·8333	0·8336	0·8173
3	...	...	...	0·9826	39	0·8343	0·8284	0·8286	0·8133
4	...	...	...	0·9770	40	0·8295	0·8235	0·8187	0·8095
5	...	...	...	0·9714	41	0·8249	0·8187	...	0·8061
6	...	...	...	0·9659	42	0·8202	0·8140	...	0·8018
7	...	...	...	0·9604	43	0·8156	0·8092	...	0·7981
8	...	...	...	0·9550	44	0·8111	0·8046	...	0·7944
9	...	...	...	0·9497	45	0·8066	0·8000	...	0·7907
10	1·0000	1·0000	...	0·9444	46	0·8022	0·7955	...	0·7871
11	0·9932	0·9929	1·0000	0·9392	47	0·7978	0·7910	...	0·7834
12	0·9865	0·9859	0·9922	0·9340	48	0·7935	0·7865	...	0·7799
13	0·9799	0·9790	0·9846	0·9289	49	0·7892	0·7821	...	0·7763
14	0·9733	0·9722	0·9764	0·9239	50	0·7849	0·7778	...	0·7727
15	0·9669	0·9655	0·9695	0·9189	51	0·7807	0·7735	...	0·7692
16	0·9605	0·9589	0·9627	0·9139	52	0·7766	0·7692	...	0·7658
17	0·9542	0·9524	0·9560	0·9090	53	0·7725	0·7650	...	0·7623
18	0·9480	0·9459	0·9493	0·9042	54	0·7684	0·7609	...	0·7589
19	0·9420	0.9396	0·9427	0·8994	55	0·7643	0·7568	...	0·7556
20	0·9359	0·9333	0·9363	0·8947	56	0·7604	0·7527	...	0·7522
21	0·9299	0·9272	0·9299	0·8900	57	0·7565	0·7487	...	0·7489
22	0·9241	0·9211	0·9237	0·8854	58	0·7526	0·7447	...	0·7456
23	0·9183	0·9150	0·9175	0·8808	59	0·7487	0·7407	...	0·7423
24	0·9125	0·9091	0·9114	0·8762	60	0·7449	0·7368	...	0·7391
25	0·9068	0·9032	0·9054	0·8717	61	..	0·7330	...	0·7359
26	0·9012	0·8974	0·8994	0·8673	62	...	0·7292	...	0·7328
27	0·8957	0·8917	0·8935	0·8629	63	...	0·7254	...	0·7296
28	0·8902	0·8861	0·8877	0·8585	64	...	0·7216	...	0·7265
29	0·8848	0·8805	0·8820	0·8542	65	...	0·7179	...	0·7234
30	0·8795	0·8750	0·8763	0·8500	66	...	0·7143	...	0·7203
31	0·8742	0·8696	0·8707	0·8457	67	...	0·7107	...	0·7173
32	0·8690	0·8642	0·8652	0·8415	68	...	0·7071	...	0·7142
33	0·8639	0·8589	0·8598	0·8374	69	...	0·7035	...	0·7112
34	0·8588	0·8537	0·8545	0·8333	70	...	0·7000	...	0·7083
35	0·8538	0·8485	0·8491	0·8292					

[1] Emeray, *Amer. Chem. J.*, 1899, **21**, 119.

Table for the Conversion of Specific Gravities, at $\frac{15°}{4°}$, into "Rational" Baumé degrees.

Sp. gr.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0·99	...	...	...	...	...	...	...	...	...	−0·018
1·00	0·126	0·270	0·414	0·557	0·700	0·843	0·986	1·128	1·270	1·412
01	1·553	1·694	1·835	1·976	2·117	2·257	2·397	2·536	2·675	2·814
02	2·953	3·091	3·229	3·367	3·505	3·643	3·780	3·917	4·053	4·189
03	4·325	4·461	4·596	4·731	4·866	5·001	5·135	5·269	5·403	5·537
04	5·671	5·804	5·937	6·070	6·202	6·334	6·466	6·598	6·729	6·860
1·05	6·991	7·122	7·252	7·382	7·512	7·642	7·771	7·900	8·029	8·158
06	8·287	8·415	8·543	8·671	8·798	8·925	9·052	9·179	9·306	9·432
07	9·558	9·684	9·809	9·934	10·059	10·184	10·309	10·433	10·557	10·681
08	10·805	10·929	11·052	11·175	11·298	11·421	11·543	11·665	11·787	11·909
09	12·030	12·151	12·272	12·393	12·514	12·634	12·754	12·874	12·994	13·114
1·10	13·233	13·352	13·471	13·590	13·708	13·826	13·944	14·062	14·179	14·296
11	14·413	14·530	14·647	14·764	14·880	14·996	15·112	15·228	15·343	15·458
12	15·573	15·688	15·803	15·917	16·031	16·145	16·259	16·373	16·486	16·599
13	16·712	16·825	16·938	17·050	17·162	17·274	17·386	17·498	17·610	17·721
14	17·832	17·943	18·054	18·164	18·274	18·384	18·494	18·604	18·713	18·822
1·15	18·931	19·040	19·149	19·258	19·366	19·474	19·582	19·690	19·798	19·905
16	20·012	20·119	20·226	20·333	20·439	20·545	20·651	20·757	20·863	20·969
17	21·074	21·179	21·284	21·389	21·494	21·599	21·703	21·807	21·911	22·015
18	22·119	22·222	22·325	22·428	22·531	22·634	22·737	22·839	22·941	23·043
19	23·145	23·247	23·349	23·450	23·551	23·652	23·753	23·854	23·955	24·055
1·20	24·155	24·255	24·355	24·455	24·554	24·653	24·752	24·851	24·950	25·049
21	25·148	25·246	25·344	25·442	25·540	25·638	25·736	25·834	25·931	26·028
22	26·125	27·222	26·319	26·415	26·511	26·607	26·703	26·799	26·895	26·990
23	27·085	27·180	27·275	27·370	27·465	27·560	27·655	27·749	27·843	27·937
24	28·031	28·125	28·219	28·312	28·405	28·498	28·591	28·684	28·777	28·869
1·25	28·961	29·053	29·145	29·237	29·329	29·420	29·512	29·603	29·694	29·785
26	29·876	29·967	30·058	30·149	30·239	30·329	30·419	30·509	30·599	30·688
27	30·777	30·866	30·955	31·044	31·133	31·222	31·311	31·400	31·488	31·576
28	31·664	31·752	31·840	31·928	32·015	32·102	32·189	32·276	32·363	32·450
29	32·537	32·624	32·711	32·797	32·883	32·969	33·055	33·141	33·227	33·312
1·30	33·397	33·482	33·567	33·652	33·737	33·822	33·907	33·991	34·075	34·159
31	34·243	34·327	34·411	34·495	34·579	34·662	34·745	34·828	34·911	34·994
32	35·077	35·160	35·243	35·325	35·407	35·489	35·571	35·653	35·735	35·817
33	35·899	35·981	36·062	36·143	36·224	36·305	36·386	36·467	36·548	36·628
34	36·708	36·788	36·868	36·948	37·028	37·107	37·187	37·267	37·346	37·425
1·35	37·504	37·583	37·662	37·741	37·820	37·898	37·977	38·056	38·134	38·212
36	38·290	38·368	38·446	38·524	38·601	38·678	38·755	38·832	38·909	38·986
37	39·063	39·140	39·217	39·294	39·370	39·446	39·522	39·598	39·674	39·750
38	39·826	39·902	39·978	40·053	40·128	40·203	40·278	40·353	40·428	40·503
39	40·578	40·653	40·727	40·801	40·875	40·949	41·023	41·097	41·171	41·245

Table for the Conversion of Specific Gravities—Continued.

Sp. gr.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
1·40	41·318	41·392	41·466	41·539	41·612	41·685	41·758	41·831	41·904	41·977
41	42·049	42·122	42·194	42·266	42·338	42·410	42·482	42·554	42·626	42·698
42	42·769	42·840	42·912	42·983	43·054	43·125	43·196	43·267	43·338	43·409
43	43·479	43·550	43·620	43·690	43·760	43·830	43·900	43·970	44·040	44·110
44	44·179	44·248	44·318	44·387	44·456	44·525	44·594	44·663	44·732	44·801
1·45	44·869	44·938	45·007	45·075	45·143	45·211	45·279	45·347	45·415	45·483
46	45·551	45·619	45·687	45·754	45·821	45·888	45·955	46·022	46·089	46·156
47	46·223	46·290	46·357	46·423	46·489	46·555	46·621	46·687	46·753	46·819
48	46·885	46·951	47·017	47·083	47·148	47·213	47·279	47·344	47·409	47·474
49	47·539	47·604	47·669	47·734	47·799	47·863	47·928	47·992	48·056	48·120
1·50	48·184	48·248	48·312	48·376	48·440	48·503	48·567	48·631	48·694	48·757
51	48·820	48·884	48·947	49·010	49·073	49·136	49·199	49·262	49·325	49·387
52	49·449	49·512	49·574	49·636	49·698	49·760	49·822	49·884	49·946	50·008
53	50·069	50·131	50·193	50·254	50·315	50·376	50·437	50·498	50·559	50·620
54	50·681	50·742	50·803	50·864	50·924	50·984	51·045	51·105	51·165	51·225
1·55	51·285	51·345	51·405	51·465	51·525	51·584	51·643	51·703	51·763	51·822
56	51·881	51·940	51·999	52·058	52·117	52·176	52·235	52·294	52·353	52·411
57	52·469	52·528	52·587	52·645	52·703	52·761	52·819	52·877	52·935	52·993
58	53·051	53·109	53·167	53·225	53·282	53·339	53·397	53·454	53·511	53·568
59	53·625	53·682	53·739	53·796	53·853	53·909	53·966	54·023	54·079	54·135
1·60	54·191	54·248	54·304	54·360	54·416	54·472	54·528	54·584	54·640	54·696
61	54·751	54·807	54·863	54·918	54·973	55·028	55·083	55·138	55·193	55·248
62	55·303	55·358	55·413	55·468	55·523	55·577	55·632	55·687	55·742	55·796
63	55·850	55·904	55·958	56·012	56·066	56·120	56·174	56·228	56·282	56·336
64	56·389	56·443	56·497	56·550	56·603	56·656	56·709	56·763	56·816	56·869
1·65	56·922	56·975	57·028	57·081	57·134	57·186	57·239	57·292	57·344	57·396
66	57·448	57·501	57·553	57·605	57·657	57·709	57·761	57·813	57·865	57·917
67	57·968	58·020	58·072	58·124	58·175	58·226	58·278	58·329	58·380	58·431
68	58·482	58·533	58·584	58·635	58·686	58·737	58·788	58·839	58·890	58·940
69	58·990	59·041	59·092	59·142	59·192	59·242	59·292	59·342	59·392	59·442
1·70	59·492	59·542	59·592	59·641	59·691	59·741	59·791	59·840	59·890	59·939
71	59·988	60·038	60·087	60·136	60·185	60·234	60·283	60·332	60·381	60·430
72	60·478	60·527	60·576	60·625	60·673	60·721	60·770	60·818	60·866	60·914
73	60·962	61·010	61·058	61·106	61·154	61·202	61·250	61·298	61·346	61·394
74	61·441	61·489	61·537	61·585	61·632	61·679	61·727	61·774	61·821	61·868
1·75	61·915	61·962	62·009	62·056	62·103	62·150	62·197	62·244	62·291	62·337
76	62·383	62·430	62·477	62·523	62·569	62·615	62·662	62·708	62·754	62·800
77	62·846	62·892	62·938	62·984	63·030	63·075	63·121	63·167	63·213	63·258
78	63·303	63·349	63·395	63·440	63·485	63·530	63·576	63·621	63·666	63·711
79	63·756	63·801	63·846	63·891	63·936	63·980	64·025	64·070	64·115	64·159
1·80	64·203	64·248	64·293	64·337	64·381	64·425	64·469	64·514	64·558	64·602
81	64·646	64·690	64·734	64·778	64·822	64·866	64·910	64·954	64·998	65·041
82	65·084	65·128	65·172	65·215	65·258	65·301	65·345	65·388	65·431	65·474
83	65·517	65·560	65·603	65·646	65·689	65·731	65·774	65·817	65·860	65·902
84	65·944	65·987	66·030	66·073	66·115	66·157	66·200	66·242	66·284	66·326
1·85	66·368	...	...	...	...	...	...	...	...	...

Special Forms of Hydrometers.

An instrument for determining the specific gravity of small quantities of liquid, called an Aero-pyknometer, has been devised by Eichhorn.[1] It is a hydrometer which contains a bulb, provided with a stopcock, between the spindle and the gravity-bob; the bulb holds 10 c.c. and is filled with the liquid under investigation. If the instrument is then immersed in distilled water at 17·5°, the specific gravity is indicated directly on the scale. A similar instrument has been described by Rubenstorff.[2]

Special hydrometers, such as alcoholometers, saccharimeters, acetometers, etc., have long been used in various industries, some of which are subject to official control. Similar instruments for the hydrometric examination of mineral acids, alkalis, and salts, made according to the most reliable tables, have been introduced by G. Muller[3]; they are not, however, in very general use. Detailed temperature correction tables for these hydrometers for nitric acid, sulphuric acid, hydrochloric acid, and ammonia, and also tables for a large number of liquids and solutions, have been compiled by P. Fuchs.[4]

Temperature Correction for Hydrometers.

For purposes of conversion of the reading of a hydrometer to the corresponding specific gravity, care must be taken that the correct conversion table is employed. The temperature for which the hydrometer is graduated is generally stated on the hydrometer, and in general, if the temperature of the liquid differs from this temperature, the necessary correction for temperature must be applied. For all temperatures higher than the standard temperature, the volume of the immersed portion of the hydrometer up to a given reading will, in general, be greater than at the standard temperature. The weight of the instrument will be the same as at the standard temperature.

Since the hydrometer readings decrease upwards from the bulb along the stem, it follows that at temperatures above the standard, the hydrometer reads high, while for temperatures below the standard the readings will be low. If t_0 = temperature at which the hydrometer readings are correct, and t = temperature at which the hydrometer is used, the real specific gravity of the liquid at t is given by

$$D_t = D\{1 - g(t - t_0)\}$$

where D is the observed specific gravity, and g the coefficient of cubical expansion of the material of the hydrometer. Using the

[1] *Ger. Pat.*, 49683.

[2] *Chem. Zeit.*, 1904, **28**, 889.

[3] *Chem. Zeit.*, 1898, **22**, 104.

[4] *Z. angew. Chem.*, 1898, **11**, 745 and 909.

value $g = 0{\cdot}000023$ as a mean value for glass, the error in the density due to a difference of temperature of 10°, between the actual and standard temperatures, is of the order of 2 parts in 10,000.

The temperature correction generally required in hydrometry is that necessary to reduce readings of a hydrometer graduated to indicate specific gravity at a specified temperature T, referred to water at a specified temperature T^1, to the basis of another hydrometer, standard temperature t, and water reference temperature t^1. The correction necessary can be determined from the following table[2]:—

Given Basis of Density.	Required Basis of Density									
	$D\frac{25^\circ}{4^\circ}$C.	$D\frac{20^\circ}{4^\circ}$C.	$D\frac{17{\cdot}5^\circ}{4^\circ}$C.	$D\frac{15{\cdot}56^\circ}{4^\circ}$C.	$D\frac{15^\circ}{4^\circ}$C.	$D\frac{15^\circ}{15^\circ}$C.	$D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ}$C.	$D\frac{17{\cdot}5^\circ}{17{\cdot}5^\circ}$C.	$D\frac{20^\circ}{20^\circ}$C.	$D\frac{25^\circ}{25^\circ}$C.
T/T¹	Δ (in units of sixth decimal place)									
$D\frac{25^\circ}{4^\circ}$C	0	+ 115	+ 172	+ 217	+ 230	+ 1104	+ 1177	+ 1459	+ 1884	+ 2931
$D\frac{20^\circ}{4^\circ}$C.	− 115	0	+ 58	+ 102	+ 115	+ 989	+ 1062	+ 1345	+ 1769	+ 2816
$D\frac{17{\cdot}5^\circ}{4^\circ}$C.	− 172	− 58	0	+ 45	+ 58	+ 932	+ 1005	+ 1287	+ 1711	+ 2758
$D\frac{15{\cdot}56^\circ}{4^\circ}$C.	− 217	− 102	− 45	0	+ 13	+ 887	+ 960	+ 1242	+ 1667	+ 2713
$D\frac{15^\circ}{4^\circ}$C.	− 230	− 115	− 58	− 13	0	+ 874	+ 947	+ 1229	+ 1654	+ 2700
$\frac{15^\circ}{15^\circ}$C.	− 1103	− 988	− 931	− 886	− 873	0	+ 73	+ 354	+ 779	+ 1826
$D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ}$C.	− 1176	− 1061	− 1004	− 960	− 947	− 73	0	+ 281	+ 706	+ 1752
$D\frac{17{\cdot}5^\circ}{17{\cdot}5^\circ}$C.	− 1457	− 1343	− 1285	− 1240	− 1227	− 354	− 281	0	+ 424	+ 1471
$D\frac{20^\circ}{20^\circ}$C.	− 1881	− 1766	− 1708	− 1664	− 1651	− 778	− 705	− 423	0	+ 1046
$D\frac{25^\circ}{25^\circ}$C.	− 2923	− 2808	− 2751	− 2707	− 2694	− 1821	− 1748	− 1468	− 1044	0

The use of the table is best explained by an example. Thus, suppose the hydrometer indicates correctly $D\frac{20^\circ}{4^\circ}$C. The correction is required in order that it shall indicate sp. gr. $D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ}$C. Corresponding to $D\frac{20^\circ}{4^\circ}$ in vertical column, and $D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ}$ horizontally, is the value + 1062. Accordingly,

$$D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ} = D\frac{20^\circ}{4^\circ} + \triangle\left(D\frac{15{\cdot}56^\circ}{15{\cdot}56^\circ}\right) \text{ where } \triangle = 0.001062.$$

[2] *U.S. Bureau of Standards, Circular No.* 19.

Thus, if the density indicated $D\frac{20^\circ}{4^\circ}$ were 1·5760, then $D\frac{15\cdot56^\circ}{15\cdot56^\circ}$ would be,

$$1.5760+(1.5760\times.001062) = 1.5760+.0017 = 1.5777.$$

When Δ is prefixed by a − sign, the corresponding correction is to be subtracted.

The scale of a hydrometer is generally printed on a paper cylinder, which is then inserted in the stem of the hydrometer. The scale is liable to move with regard to the stem, and for this and other reasons, hydrometers in actual use should be checked either by comparison with reliable standard instruments, graduated in real specific gravities, or by a comparison of the specific gravity of a liquid as determined by the pyknometer or "sinker" method, with the value as determined by the hydrometer.

The Second International Congress of Applied Chemistry (1896) passed the following resolutions regarding hydrometers:—

1. The scales should be either in specific gravities, or in degrees Baumé, Brin, Balling, etc. The relation of the degrees of the specific gravities are to be determined by an International Committee.

2. For liquids with different capillary properties, special hydrometers, graduated accordingly, should be used; otherwise corresponding corrections must be made.

3. Readings should, as a rule, be taken at the intersection of the surface of the liquid with the stem of the hydrometer, without regard to the meniscus. In the case of opaque liquids, where this is impossible, the readings of a hydrometer which has not been specially calibrated for such liquids must be corrected to give readings corresponding to the actual surface of the liquid.

4. Hydrometers should be provided with a centigrade thermometer, graduated from zero point.

5. One end of the spindle should be provided with a mark coinciding with the final graduation of the scale, in order to be sure that the scale does not change its position.

6. The total errors of a hydrometer should not be greater than one graduation of the scale.

Calibration of Hydrometers.

For purposes of calibrating the readings of hydrometers, it is very desirable that a reliable and accurate method for the determination of specific gravity should be available. Such a method is provided by the use of the pyknometer. The most convenient form of pyknometer is shown in Fig. 60. The weight of water and of the liquid whose specific

gravity is to be determined, respectively required to fill the pyknometer between the mark A and the end of the limb B, is ascertained, the temperature in each case being adjusted to any given value by immersing the pyknometer and its contents in a bath at the desired temperature. Excess liquid is removed from the limb B by touching the end of B with blotting-paper. According to Ostwald, determinations of specific gravity by means of a pyknometer can be made with the following accuracy:—

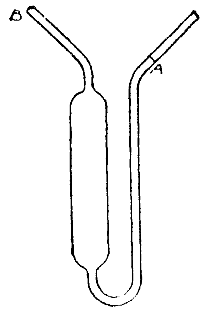


FIG. 60.

Volume of Pyknometer	Probable Error
5 c.c.	±.0001
25 c.c.	±.00002
200 c.c.	±.000002

When a volatile liquid is used in the pyknometer, the latter is provided with caps at the ends of the limbs.

If the pyknometer is filled with liquid at temperature t_1, and with water at temperature t_0, and if

W_0 = Weight of pyknometer empty,
W_1 = Weight of pyknometer + water,
W_2 = Weight of pyknometer + liquid,

all weights being corrected for buoyancy of air, Δ = Density of water at t_0, then specific gravity of liquid,

$$D\frac{t_1}{4} = \frac{W_2 - W_0}{W_1 + W_0} \cdot \Delta\{1 - \gamma(t_1 - t_0)\}$$

where γ = coefficient of cubical expansion of the material of the pyknometer, and equals 0·000023 for ordinary soft glass.

Ostwald has pointed out that in very exact measurements of specific gravity by means of the pyknometer, attention must be paid to the fact that the glass after expansion by heat does not immediately resume its original volume on cooling. He therefore advises avoiding the application of heat for cleaning purposes, and suggests that the pyknometer should be cleaned by treatment successively with water, alcohol or ether, the latter being rapidly removed by a current of air. Care must be taken that the ether leaves no residue on evaporation.

The Westphal balance is frequently employed for the determination of the specific gravity of liquids, and as modified by Mohr can be used for solids and liquids. The Westphal balance is shown in Fig. 61. The plummet employed consists of a mercurial thermometer enclosed in a glass case, and this is suspended from the right arm of the balance. The beam is first counterpoised, so that the balance is in equilibrium

when the plummet is sunk in distilled water, by placing riders in suitable notches in the beam as shown. When the plummet is immersed in liquids of other densities, the weights are adjusted until equilibrium is restored. The weights of the various riders are so adjusted that the density of the liquid can then be read off directly. Mohr's modification is shown in Fig. 62. The plummet together with the suspending platinum wire weighs 15 g., and the displacement of its volume is equal to 5 g. of distilled water at 15°. Riders are provided whose respective weights are 5 g., 0·5, 0·05 and 0·005 g. respectively. To use the balance, the larger rider is put on

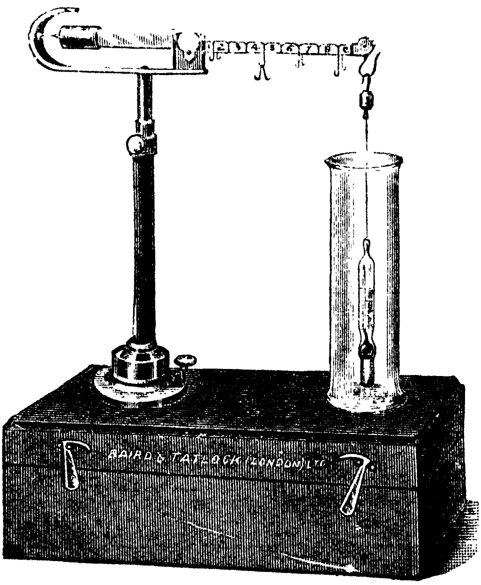


FIG. 61.

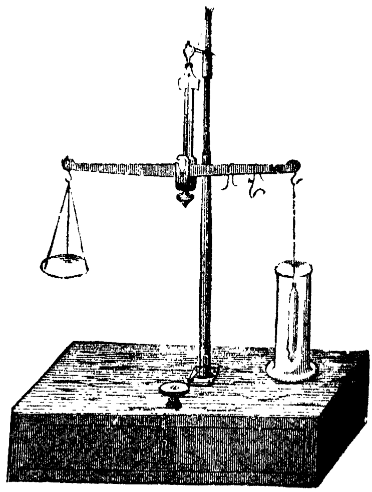


FIG. 62.

the same hook with the plummet, and the latter immersed in distilled water, when equilibrium is restored: in this position the platinum wire twisted round the top of the plummet is below the surface of the water. If the liquid whose density is required is lighter than distilled water, when the plummet is immersed in it, the large rider must be placed on the divided beam, so that equilibrium is restored. Should the large rider require to be placed between two notches for this purpose, it is placed on the notch of lower value, and then the next smaller rider employed in like manner. Should the position of the second rider fall between two notches, it is likewise placed in the lower valued notch, and succeeding riders employed in the same manner until equilibrium is restored. Should two riders be required at the same notch, the smaller is suspended from the larger. The

specific gravity of the liquid is then read off directly to the fourth decimal place from the divided beam. If a liquid heavier than distilled water is tested, the process is as described, except that one of the large riders is hung from the hook with the plummet, while the others cross the beam at their respective appropriate notches.

Flotation Method for Determining Specific Gravities.

When the liquid whose specific gravity is required is available in exceedingly small quantity, the best method is to determine a mixture of liquids (*e.g.*, alcohol and water) in which the liquid is insoluble, in such proportion that the density of the mixture is equal to that of the liquid. Having found liquids in which the given liquid is insoluble, a series of mixtures of these is made, and, by trial, two adjacent members of the series are determined, such that a drop of the given liquid released from a fine tube under the surface of the mixture descends in the one and ascends in the other. The relative proportions of the constituents of the mixture are then adjusted, until the given liquid when introduced below the surface at any depth remains stationary. The specific gravity of the mixture is then ascertained by any of the preceding methods, and is equal to the specific gravity of the liquid in question. Care must be taken that no air bubbles are attached to the drop of liquid when introduced into the liquid mixture.

A similar method can be applied for the determination of the specific gravity of solids of which very small quantities only are obtainable. The following liquids of high specific gravity are useful for this purpose :—

Substance.	Solvent.	Maximum density of Solution.
Double Iodide of Potassium and Mercury	Water	3·196
Cadmium Borotungstate	,,	3·281
Mercuric and Barium Iodides . . .	,,	3·588
Methylene Iodide	Benzene	3·33

Determination of Specific Gravity by Use of a Sinker.

The specific gravity of a liquid can be very accurately determined by means of a sinker, provided the liquid is not too volatile, and is obtainable in sufficient quantity. A glass sinker containing mercury or lead shot is made of the form shown in Fig. 63. This sinker is

suspended from one arm of the balance by means of a fine platinum wire and its weight ascertained—

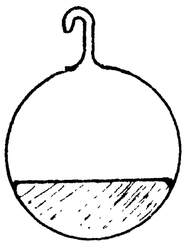


FIG. 63.

(1) in air $= W_0$
(2) in water at temp. $t_0 = W_1$
(3) in the liquid at temp. $t_1 = W_2$

then the specific gravity of the liquid—

$$D\frac{t_1}{4} = \frac{W_0 - W_2}{W_0 - W_1} \cdot \Delta\{1 - \gamma(t_1 - t_0)\}$$

where Δ = density of water at t_0, and γ = coefficient of cubical expansion of the material of the sinker = 0·000023 for glass.

Calibration of Sinker.—Provided the weighings in the liquid and water are made at the same temperature, which temperature is used throughout as a standard temperature for all liquids—

$$D\frac{t_1}{4} = \frac{W_0 - W_2}{W_0 - W_1}\Delta$$

$$= -\frac{\Delta W_2}{W_0 - W_1} + \frac{\Delta W_0}{W_0 - W_1}.$$

The curve giving the relation between $D\frac{t_1}{4}$ and W_2 is therefore a straight line, and this straight line being drawn for a sinker, the specific gravity of any liquid can be read off directly when the

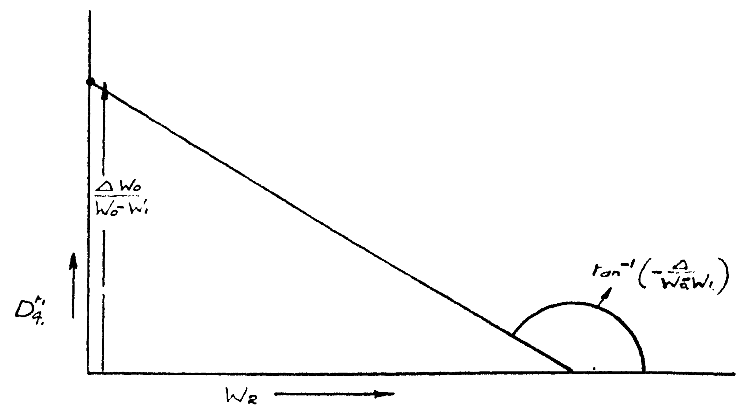


FIG. 64.

appropriate value of W_2 has been ascertained. The straight line can be drawn from the values of W_2 appropriate to two values of $D\frac{t_1}{4}$, or can be drawn as shown in Fig. 64. The specific gravity corresponding to any ascertained value of W_2 can then be directly read from the straight line graph.

In carrying out determinations of specific gravity by this method capillary effects produced at the point where the platinum suspension wire cuts the surface of the liquid reduce the sensitiveness of the balance very considerably. This disturbing factor can be reduced by coating the wire with platinum grey, as suggested by Kohlrausch.[1] The platinum grey is produced by making the platinum wire the kathode, in a 3 per cent. solution of platinic chloride containing a trace of lead acetate. Another piece of platinum wire is used as anode, and current from a battery of about 4 volts E.M.F. is passed

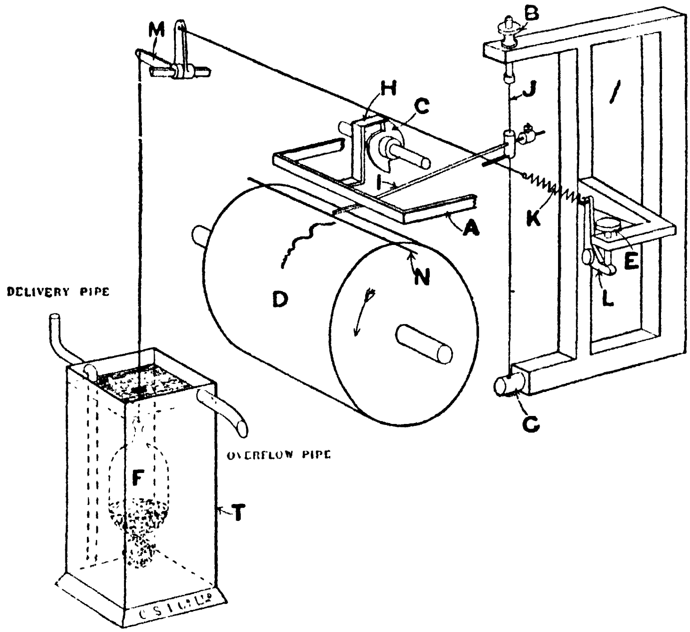


FIG. 65.

until the kathode is coated with platinum black. The wire is then removed and heated in a Bunsen flame to redness.

The sinker method has been applied by the Cambridge and Paul Scientific Instrument Company to the construction of a recording densimeter, whereby a continuous record is obtained of the density of a liquid (see Fig. 65). The sinker F is suspended by a fine platinum wire in such manner as to be totally immersed in the liquid in question. The suspended wire is connected to the bell crank lever M, the movements of which are transmitted to the boom I. This boom is attached to a vertical steel wire J and counterpoised by a weight. The movements of the boom are conditioned by the resistance to torsion of the steel wire, and also by the

[1] *Ann. Physik*, 56, p. 185.

helical spring K. The boom I swings above the drum D of a thread recorder. The drum rotates at a predetermined rate and carries the recording paper. A clock-driven cam operates the cam wheel C, and the presser bar A is depressed at intervals of half a minute or one minute. The presser bar depresses the inked thread on the recording paper at these intervals, so that a record in the form of a series of dots practically forming a continuous line is obtained. In the intervals between the depression of the bar, the pointer is free to take up another position. Ordinarily a full scale deflection of 80 mm. corresponds to a change of 2·5 per cent. in the density of the solution. The record sheet can be calibrated to read directly in terms of specific gravity.

In another form, employing two sinkers of exactly the same volume, the one immersed in the solution, a record of whose density is required, and the other in water at the same temperature, the effect of temperature changes is eliminated.

Coefficients of Expansion of Liquids: Absolute and Apparent

The value of the coefficient of expansion of a liquid is frequently required in chemical technology, as it enables the value of the specific gravity of the liquid to be corrected to any desired temperature. Moreover, a knowledge of its magnitude is of especial importance in calculating the allowance to be made for expansion space in transport and storage vessels. The coefficient of expansion can be most accurately determined by means of the pyknometer.

The weight of liquid filling the pyknometer at temperature t_1, is ascertained and found to be $(M+m)$.

The weight of liquid filling the pyknometer at some higher temperature, t_2 is likewise determined and found to be M. It follows, therefore, that if $\rho =$ the density of the liquid at t_1, since a mass $(M+m)$ fills the pyknometer at temperature t_1

$$\frac{M+m}{\rho} = V,$$

V being the volume of the pyknometer at t_1.

In like manner, if $E =$ coefficient of absolute expansion of the liquid, and $g =$ the coefficient of expansion of the material of the pyknometer,

$$\frac{M}{\rho}\{1+E(t_2-t_1)\} = V\{1+g(t_2-t_1)\}$$

Hence $$\frac{M\{1+E(t_2-t_1)\}}{M+m} = 1+g(t_2-t_1)$$

$$\therefore \quad E = \frac{m}{M(t_2-t_1)} + g\left(\frac{M+m}{M}\right).$$

It must be noted that when a liquid is contained in a vessel, any expansion of the liquid is accompanied by an expansion of the vessel. The apparent expansion of the liquid is for this reason less than its absolute expansion, and for storage and transport purposes it is this apparent expansion that is important. The coefficient of apparent expansion A, is given by $\frac{m}{M(t_2 - t_1)}$. (*N.B.* M = weight of liquid filling pyknometer at *upper* temperature t_2.)

$$E = A + g\frac{M+m}{M}.$$

As, in general, m is small compared with M, the above equation may be written:—

$$E = A + g.$$

If the pyknometer be of quartz, $g = o$ (very nearly) and E = A.

The coefficient of expansion of the liquid can also be accurately determined by ascertaining the specific gravity of the liquid by the sinker method at two temperatures, temperature corrections being applied as already explained (p. 129). The difficulty of maintaining the liquid at any desired temperature is reduced if one chosen temperature is, if possible, 0°, and the other atmospheric temperature. The readings of specific gravity may then be made by the hydrometer, the precautions already specified and the corrections enumerated being applied in every case.

ρ_{t_1} being the specific gravity at t_1, and ρ_{t_2} the specific gravity at t_2, E the coefficient of absolute expansion,

$$\frac{1}{\rho_{t_2}} = \frac{1}{\rho_{t_1}}\{1 + E(t_2 - t_1)\} \quad \text{giving} \quad E = \frac{\rho_{t_1} - \rho_{t_2}}{\rho_{t_2}(t_2 - t_1)}.$$

The coefficient of expansion is also determined by the dilatometer. An apparatus which allows for the simultaneous examination of eight samples has been devised by Holde. The dilatometers (Figs. 66, 67, and 68) have the shape of bulbs of about 30 c.c. capacity with graduated stems. The initial volume of liquid is adjusted in a large water bath as shown in Fig. 67. For higher temperatures, the water bath B is placed in a vapour bath heated by a Bunsen burner. The vapourising liquid is chosen according to the temperature to be attained in the bath. Reflux condensation is provided for at *e*. A number of dilatometers, together with a thermometer graduated to tenths of a degree, are suspended by means of rubber rings in the bath. Fig. 68 shows the method of charging the dilatometers with the liquid by suction with a capillary tube. The stems of the dilatometers are carefully calibrated with the aid of mercury. The volume up to the zero mark is determined by weighing the dilatometer filled up to the zero with

water at an ascertained temperature, the weighings being reduced if necessary to *vacuo*. The coefficient of expansion is given by

$$E = \frac{V_2 - V_1}{V_1(t_2 - t_1)} + g$$

where V_2 and V_1 are the volumes at $t_2°$ and $t_1°$ respectively, and g

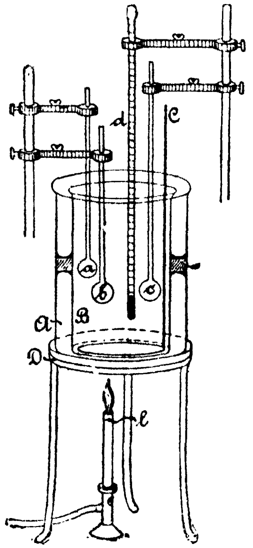


FIG. 66.

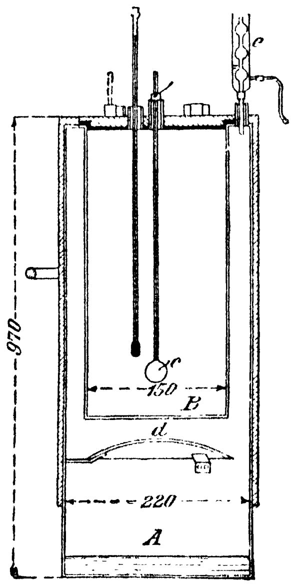


FIG. 67.

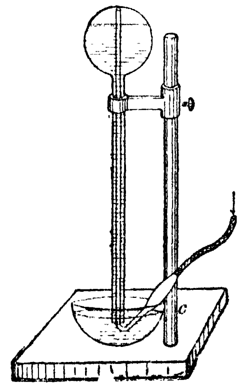


FIG. 68.

is the coefficient of expansion of the material of the dilatometer. The value of the coefficient of cubical expansion E having been determined, the correction of the specific gravity of the liquid to any desired temperature is given by

$$D_2 = \frac{D_1}{\{1 + E(t_2 - t_1)\}} = D_1\{1 - E(t_2 - t_1)\}$$

where D_2 and D_1 are the respective specific gravities at temperatures t_2 and t_1, the specific gravity in each case being in terms of water at a single temperature, such as 15°. If the density D_2 is to be expressed in terms of water at t_2, the further correction on p. 117 must be introduced.

RELATIVE DENSITY OF GASES

For gases, the term density or relative density is more commonly used than the term specific gravity. By the absolute density of a gas is meant the mass of unit volume (1 c.c.) of the gas measured under standard conditions of temperature and pressure (0° C. and 760 mm.

mercury pressure). In technical practice the measurement of absolute density of a gas is seldom called for, and the relative density of a gas is what is practically always required. By relative density is meant the ratio of the weight of a given volume of the gas to the weight of an equal volume of air (or hydrogen) measured under the same conditions of temperature and pressure. All gases follow very closely the two gas laws, viz.:—

The Law of Charles: the volume of a given mass of gas under constant pressure is proportional to the absolute temperature of the gas; and

Boyle's Law: the volume of a given mass of gas at constant temperature is inversely proportional to the pressure to which the gas is subjected.

As a consequence of Charles's Law, it is obvious that in the case of a gas, the relative density of the gas being measured in terms of air (or hydrogen) under the same conditions of temperature and pressure, the relative density is independent of these conditions. If the value of the density of the gas under various conditions of temperature and pressure is to be expressed in terms of air (or hydrogen) at any fixed temperature and pressure, the calculation is made by means of the relation,

$$\frac{P_1}{D_1T_1} = \frac{P_2}{D_2T_2}$$

where D_1 is the relative density of the gas under conditions of pressure and absolute temperature represented by P_1 and T_1, the suffix 2 having similar reference to the conditions represented by D_2, P_2, T_2. Thus, if the density of coal gas at 15° and 760 mm. pressure is 0·430 (measured in terms of air at 15° and 760 mm. pressure), then at 30° and 780 mm. pressure the density of the coal gas in terms of air at 15° and 760 mm. pressure would be D_2, given by

$$\frac{760}{0.430 \times (273+15)} = \frac{780}{D_2(273+30)}$$

giving $$D_2 = \frac{0.430 \times 780 \times 288}{760 \times 303} = 0.420.$$

Chemical theory indicates that if the relative density of a gas be expressed in terms of hydrogen (under the same conditions of temperature and pressure), then the molecular weight of the gas is represented by twice the density (relative to hydrogen). It was customary up to a few years ago, to express the atomic weights of the elements in terms of hydrogen = 1. The atomic weight of oxygen on this basis is 15·901. At the present time, the international atomic weights are expressed in terms of oxygen = 16, and the relative densities of various gases are

frequently expressed in terms of oxygen = 1. The following table contains values of the densities (relative and absolute) of various gases :—

Gas.	Molecular Formula.	Molecular Formula Weight O = 16	Weight in grams of one litre of gas				Relative Density of Dry Gas		
			Dry		Saturated with water vapour				
			At 0° C. & 760 mm.	At 15° C. & 760 mm.	At 0° C. & 760 mm.	At 15° C. & 760 mm.	Air = 1	Oxygen = 1	Hydrogen = 1
Acetylene .	C_2H_2	26·02	1·181	1·120	1·179	1·114	0·914	0·826	13·14
Ammonia .	NH_3	17·03	0·7708	0·7307	0·7711	0·7312	0·5962	0·5394	8·577
Benzene .	C_6H_6	78·05	3·486	3·304	3·470	3·261	2·696	2·438	38·79
Butane .	C_4H_{10}	58·08	2·599	2·464	2·589	2·436	2·010	1·819	28·92
Butylene .	C_4H_8	56·06	2·504	2·373	2·494	2·346	1·937	1·752	27·87
Carbon Bisulphide	CS_2	76·14	3·401	3·224	3·386	3·183	2·631	2·380	37·84
Carbon Dioxide .	CO_2	44·00	1·9768	1·8738	1·970	1·854	1·5291	1·3833	21·996
Carbon Monoxide	CO	28·00	1·2504	1·1854	1·248	1·178	0·9672	0·8750	13·913
Chlorine .	Cl_2	70·92	3·221	3·053	3·207	3·015	2·492	2·254	35·84
Cyanogen .	$(CN)_2$	52·02	2·336	2·215	2·327	2·191	1·807	1·635	25·99
Ethane .	C_2H_6	30·05	1·356	1·286	1·353	1·277	1·050	0·949	15·09
Ethylene .	C_2H_4	28·03	1·261	1·196	1·258	1·189	0·975	0·882	14·03
Hydriodic Acid . .	HI	127·93	5·659	5·364	5·630	5·285	4·377	3·960	62·97
Hydrobromic Acid .	HBr	80·93	3·505	8·322	3·488	3·277	2·711	2·453	39·00
Hydrochloric Acid .	HCl	36·47	1·6398	1·5544	1·634	1·541	1·2684	1·1475	18·246
Hydrocyanic Acid	HCN	27·02	1·206	1·143	1·204	1·137	0·933	0·844	13·42
Hydrogen	H_2	2·016	0·08987	0·08519	0·09433	0·09654	0·06952	0·06289	1·0000
Hydrogen Sulphide .	H_2S	34·08	1·538	1·458	1·534	1·447	1·190	1·076	17·11
Methane .	CH_4	16·03	0·7168	0·6798	0·7178	0·6808	0·5545	0·5016	7·976
Nitric Oxide	NO	30·01	1·3402	1·2704	1·337	1·262	1·0367	0·9379	14·913
Nitrogen .	N_2	28·02	1·2507	1·1856	1·248	1·179	0·9674	0·8752	13·917
Nitrogen* (atmospheric)	...	...	1·2566	1·1912	1·254	1·185	0·9720	0·8794	13·983
Nitrous Oxide .	N_2O	44·02	1·9777	1·8747	1·971	1·854	1·5298	1·3840	22·008
Oxygen .	O_2	32·00	1·4290	1·3546	1·426	1·344	1·1105	1·0000	15·901
Ozone . .	O_3	48·00	2·144	2·033	2·136	2·012	1·666	1·500	23·85
Pentane .	C_5H_{12}	72·10	3·220	3·052	3·206	3·014	2·491	2·253	35·83
Propane .	C_3H_8	44·07	2·020	1·915	2·013	1·897	1·563	1·414	22·48
Propylene .	C_3H_6	42·05	1·937	1·836	1·931	1·818	1·498	1·355	21·55
Sulphur Dioxide .	SO_2	64·07	2·9266	2·7742	2·913	2·739	2·2638	2·0480	32·565
Air . . .	...	...	1·2928	1·2255	1·2899	1·2177	1·0000	0·9047	14·385

* One litre of "atmospheric nitrogen" contains 988·14 c.c. of pure nitrogen and 11·86 c.c. of argon.

The absolute values of densities at 0° and 760 mm. (dry) are experimental values. The relative densities are expressed in terms of the respective standards at 0° and 760 mm. Departures of the gases from the laws of Boyle and Charles will necessitate the introduction of corrections into the values of the relative densities at other

temperatures and pressures. For the permanent gases, the necessary corrections are small and for technical purposes negligible. The densities of the gases saturated with water vapour are given under a total pressure of 760 mm., *i.e.*, partial pressure of gas + partial pressure of water vapour = 760 mm.

The specific gravity of a gaseous mixture can be calculated from its percentage composition. The following will illustrate the method in the case of a sample of coal gas:—

	Percentage by Volume.		Sp. gr. relative to Air at 0° C. and 760 mm.	Product.
CO_2 . .	1.2	×	1.529	1.835
C_nH_m . .	3.4	×	1.498	5.093
O_2 . .	0.3	×	1.110	0.333
CO . .	6.8	×	0.967	6.576
CH_4 . .	32.9	×	0.554	18.227
H_2 . .	49.2	×	0.0695	3.419
N_2 . .	6.2	×	0.967	5.995
	100.0			41.478

The specific gravity of the dry gas at 0° and 760 mm. would therefore be 0.415 relative to air at the same temperature and pressure. The usual approximate assumption is made in this calculation that the unsaturated hydrocarbons present in the gas are equivalent to an equal volume of propylene. The relative specific gravity of the dry or moist gas under any other conditions of temperature and pressure can now be calculated in the usual manner. In the case of moist gas, the percentage saturation with moisture at the temperature in question must be known, and also the pressure of water vapour at this temperature. This latter can be obtained from a table of physical constants. The mass of the vapour required to saturate a given volume of a neutral gas at a given temperature, is calculated from the vapour pressure by the formula—

$$p = \frac{6229gT}{m\left\{v + 6229\frac{gT}{mb}\right\}}$$

where p = the vapour pressure of the vapour in cms. of mercury at absolute temperature T° C.

g = the weight of vapour in grams to saturate a volume v c.c. of the neutral gas.

m = the molecular weight of the vapour.

b = total pressure to which the gas is subjected (in cms. of mercury).

Determination of the Relative Densities of Gases by the Method of Effusion.

In technological practice the relative densities of gases are almost invariably determined by methods dependent upon the law of diffusion of gases. It follows as a consequence of the kinetic theory of gases, and the fact has been established by numerous experiments, that the density of a gas is proportional to the square of the time of effusion of a constant volume through a small orifice. The theory assumes the flow of the gas through the orifice to be isothermal, and that there is no loss of energy due to friction. If, therefore, t_1 and t_2 be the respective times of effusion of equal volumes of two gases of densities ρ_1 and ρ_2 respectively through a small orifice in a thin plate,

$$\frac{\rho_1}{\rho_2} = \frac{t_1^2}{t_2^2}$$

The theory of the method, the necessary precautions, etc., have been very thoroughly studied by Edwards.[1]

The first apparatus employing this method was described by Bunsen.[2] Schilling's apparatus[3] (Fig. 69) is a development of Bunsen's apparatus, and has now completely displaced the latter.

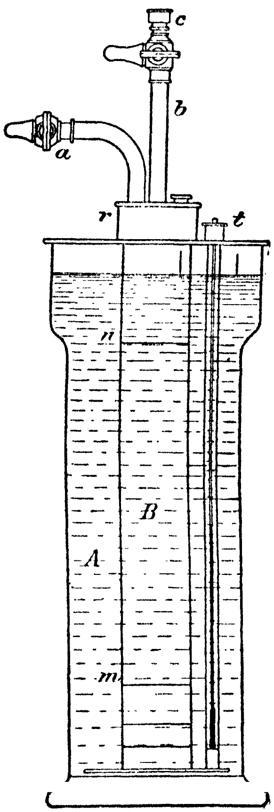


FIG. 69.

The apparatus consists of a large glass cylinder A about 40 cm. high, in which a smaller cylinder B is suspended and kept in position at the top by the metal frame *r*, which rests with three arms on the rim of the cylinder and also carries the thermometer *t*. B is open at the bottom and is fixed just free from the base of A, where it is again centred by a metal frame with three arms. The tubes *a* and *b* fixed on the metal frames are provided with stopcocks, and serve for the admission and expulsion of the gas. A three-way stopcock can be turned so as to communicate either with *b* or *c*. The headpiece *c* is fitted with a small thin platinum disc placed horizontally with a fine opening in the middle, which is made by piercing the foil with a needle and then

[1] Technologic Paper No. 94, Bureau of Standards, Washington, 1917.

[2] *Gasometrische Methoden*, 1857, pp. 121-127, and 3rd edition, 1877, p. 184.

[3] *Handbuch für Gasbeleuchtung*, 3rd edition, p. 101.

removing all roughness from the orifice. To protect it from dust, etc., a cap is screwed on the head *c* when the apparatus is not in use.

For the determination, the vessel A is filled with so much water that there is just sufficient room for the introduction of the cylinder B when filled with air and suspended therein. As soon as the water has come to rest, the time of effusion of the volume of air between the marks *m* and *n* is determined; these marks go right round the cylinder; according to Pannertz, bands of fine cord round the marks permit of greater accuracy of observation. The stopcock on *b* is first turned so as to communicate with the head *c*; the level of the water in the lower part of the cylinder then begins to rise as it displaces the air, and the time is taken with a stop-watch as soon as the meniscus passes the mark *m*; a similar reading is taken when the meniscus of the water passes *n*, and the time for effusion of air is given by the difference. The residual air in the cylinder is then displaced by the gas to be examined by connecting the stopcock *a* with the supply, and opening *b*; the gas is allowed to pass through for about two minutes. The displacement of the air is accelerated by raising the cylinder almost completely out of the water and lowering it again. The outlet of *b* is then closed, the cylinder again raised in order to fill it completely with gas, the inlet of *a* closed and the cylinder again placed in position. After the water has come to rest the time of effusion of the gas is measured under exactly the same conditions as with the air, so that the times of effusion of equal volumes of gas and air, measured between *m* and *n*, are ascertained. The respective times for air and the gas being t_a and t_g, ρ_a and ρ_g being the respective densities of air and gas at the temperature of the experiment,

$$\rho_g = \frac{t_g^2}{t_a^2}\rho_a$$

It must be noted that, in each case, the air and gas are saturated with water vapour, and the respective densities ρ_a and ρ_g are consequently the densities of the *moist* air and gas. The density of air saturated with water vapour at any temperature can be calculated from the corresponding density of dry air at the same temperature by the expression:

$$\rho_{ma} = \frac{\rho_{da}(\mathrm{H} - \cdot 378p)}{\mathrm{H}}$$

where ρ_{ma} and ρ_{da} are the respective densities of moist and dry air at a pressure of H mm., the barometric pressure, and p is the saturation vapour pressure of water vapour in mm. at the temperature of the experiment. Values of ρ_{da}, ρ_{ma}, and p will be found in Kaye and Laby's *Tables of Physical and Chemical Constants*, 4th edn., pp. 27 and 42 respectively. The absolute density of the moist gas can thus be ascertained.

In any actual experiment the respective times should be taken as the mean of the times determined by three experiments with the respective gases, and as the times enter into the expression for the ratio of the densities in the form of t^2, the times must be determined with an accuracy of 1 part in 1000 if an accuracy of 1 part in 500 is required in the result. This is in accordance with the above equation as it follows by differentiation, that:—

$$\frac{d(\rho_g)}{\rho_g} = \frac{2(dt_g)}{t_g}$$

and
$$\frac{d(\rho_g)}{\rho_g} = -\frac{2dt_a}{t_a}.$$

With a time of efflux of the order of 1 minute, a measurement of the time correct to 0·1 second will permit an accuracy of 1 part in 300 to be obtained in the value of the specific gravity. This accuracy is not generally attained with any technical form of effusion apparatus for the determination of the specific gravity of gases. According to Edwards (*loc. cit.*) an accuracy of 2 per cent. is possible after standardisation of the effusion orifice, if various precautions are taken. Without such standardisation, with certain conditions of use, errors as large as 30 per cent. are possible by the use of an effusion type of apparatus.

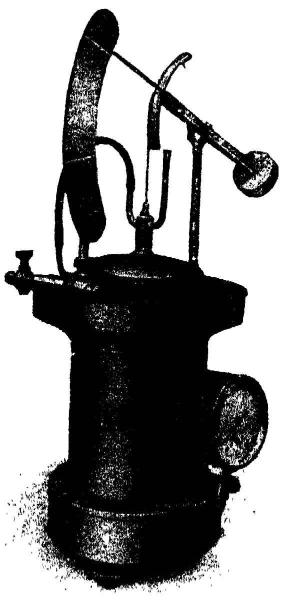


Fig. 70.

A Specific Gravity Bell depending on the same principle as the above apparatus is made by Messrs Alex. Wright & Co., Westminster (Fig. 70). The bell is suspended from a balance beam in a small water tank. The crown of the bell is drawn out so that a standpipe may be brought up above the water level, although the bell itself is submerged. Attached to the crown is a plate in which a fine effusion hole is drilled, and this is protected by a cap. Extending from the beam is a pointer, and the time of effusion with any gas is ascertained by noting the interval between passage of the pointer over two marks upon a vertical plate. With care the apparatus can be made to yield values for the relative specific gravity of moist gases correct to 0·5 per cent. The apparatus is portable and readings can be quickly made.

A form of Schilling's apparatus is sometimes employed as a gas purity meter. The theory of the instrument is exactly the same as

that already explained, variations of the density of the gas producing an alteration in the time of the efflux of the gas from the apparatus. In the case of an extremely light gas such as hydrogen, the presence of a very small proportion of another gas can be detected by this method. Other physical methods dependent upon the physical properties of hydrogen, such as its thermal conductivity, are also available for this purpose.

The Lux Balance[1] is sometimes used in gas works practice, and it possesses the advantage that it indicates the specific gravity of the gas directly. Its action depends on the simple principle of directly weighing equal volumes of air and gas, the difference in weight being shown as specific gravity by the displacement of a pointer on a scale. A table supplied with the apparatus gives the temperature and pressure corrections from 0° to 30°, and from 730 mm. to 790 mm. The apparatus is not an easy one to work with, and care is necessary

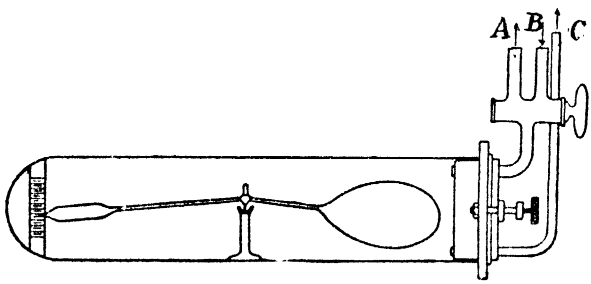


FIG. 71.

if values of the density are to be obtained correct to the second place of decimals.

A more accurate and convenient type of balance for the determination of the specific gravity of gases has been described by the United States Bureau of Standards, 1917.[2] The balance is based on Archimedes' principle, namely, that when a body is weighed in a fluid, the apparent loss of weight of the body (compared with its weight *in vacuo*) is equal to the weight of the fluid displaced by the body. Furthermore, in the case of a gas, the weight of the gas displaced by a body of definite volume is proportional to the density of the gas, which is itself proportional to the pressure of the gas. The balance is shown in Fig. 71. Then balance-case is made gas-tight. The beam consists of a rod about 1·5 mm. in diameter, to one end of which a light glass or metal globe is attached. Two tubes pass into the balance-case: the one, fitted with a two-way cock, connects either with a vacuum pump or the gas supply, the other to a mercury-filled U-gauge. A change of pressure of the air in the case, equivalent to a few tenths of a mm.

[1] *J. Gasbeleucht.*, 1887, **35**, 251. [2] See also *Gas J.*, 1917, **137**, 115.

of mercury, should produce a measurable change in the point of equilibrium of the pointer. The equilibrium position is read on a small scale or by reference to the cross-wire of a reading telescope. With dry air in the case, the pressure is adjusted until the pointer attains the position of equilibrium. The case is then exhausted of air, and the gas, whose density is required, admitted in a dry state. The pressure of the gas is adjusted until the pointer once more attains its position of equilibrium. If P is the atmospheric pressure (any variations of which during the determination are of course taken into account), p_a the excess pressure in the case of air, p_g the excess pressure in the case of gas in question, then :—

Density of the gas in question under pressure $P+p_g$

$$= \text{Density of air under pressure } P+p_a$$

$$= \rho_a \frac{P+p_a}{P} \text{ where } \rho_a = \text{density of air under atmospheric pressure P.}$$

Density of the gas under pressure P

$$= \rho_a \frac{P+p}{P} \times \frac{P}{P+p_g}$$

if ρ_g = density of the gas under pressure P (atmospheric pressure)

$$\frac{\rho_g}{\rho_a} = \frac{P+p_a}{P+p_g}.$$

The method is accurate to about 0·2 per cent., and the apparatus is light, portable, and durable. It has the added advantage, compared with some types of effusion apparatus, that the density of dry gases can be readily determined.

Threlfall[1] has described a method for the comparison of the specific gravities of two gases based on the measurement of the difference of pressure due to columns of equal lengths of the gases. The difference of pressure is ascertained by means of a delicate micromanometer, and the attainable accuracy is about 1 part in 5000 using columns of the gases, 20 metres long. The method can be made recording as suggested by Threlfall. A similar method has been devised by Krell[2] and by the Fuel Research Board.[3]

A recording "Gravitometer" has been designed by Messrs Alex. Wright & Co., Westminster.[4] The instrument is based upon the fact that the pressure exerted upon any surface exposed to a column of gas is proportional to the density of the gas. The variation of the pressure determines the position of a pointer which can be made to yield a permanent record on a chart driven by clockwork.

[1] *J. Soc. Chem. Ind.*, 1907, **26**, 359.
[2] *J. Gasbeleucht.*, 1899, **42**, 212.
[3] Technical Paper No. 5, Fuel Research Board.
[4] *Gas J.*, 1912, 958 ; *ibid.*, 1914, **126**, 115.

Specific Gravity of Solids.

The simplest direct method for the determination of the specific gravity of a solid heavier than water consists in weighing the body in air and then in water at a definite temperature. The suspending wire, if of platinum, should be treated as already explained (see p. 133). The apparent loss of weight, when weighed in water, is the weight of a volume of water equal to the volume of the body.

If then :—

W_0 = Weight of the body in air at t_0
and W_1 = Weight of the body in water at temp. t_1

then sp. gr. of the body at t_0

$$\frac{W_0 D}{W_0 - W_1} + \sigma \left\{ 1 - \frac{W_0}{W_0 - W_1} \right\}$$

where D is the density of the water at temperature t_1 and σ is the density of the air at t_0. In the case of a solid lighter than water, a similar method can be applied, a sinker being attached to the body when weighed in water and determinations being made of :—

1. The weight of the body in air = W_0.
2. The weight of the body and sinker in water = W_1.
3. The weight of the sinker alone in water = W_2.

The sp. gr. of the solid is :—

$$= \frac{W_0 D}{W_0 - W_1 + W_2} + \sigma \left\{ 1 - \frac{W_0}{W_0 - W_1 + W_2} \right\}$$

where D and σ have the same significance as previously. Generally, the term involving σ is small, and therefore neglected in these expressions.

If the densities of a large number of various substances have to be determined, it is desirable to have one or more sinkers whose weights in water at any definite temperature are known. The work can in this way be very considerably expedited.

In the case of solids, soluble in water or which are acted upon by water, another liquid of known density, such as benzene, must be employed, if this method is used.

The specific gravity of a solid in the form of a fine powder can be determined by means of the specific gravity bottle. The bottle is first weighed empty. The weight of water filling the bottle at some measured temperature is then ascertained. For this purpose the bottle is filled with water while immersed in a bath of water at a definite temperature, and then weighed. The bottle is then emptied, dried, about half filled with the powder in question, and the whole weighed. The weight of powder is thus ascertained. The bottle, still containing

the powder, is now filled as regards the remaining space with water and again weighed. If then :—

W_0 = Weight of bottle.
W_1 = Weight of bottle and water to mark.
W_2 = Weight of bottle and powder.
W_3 = Weight of bottle, powder, and water to mark.

Sp. gr. of powder

$$= \frac{(W_2 - W_0)D}{(W_1 - W_0) - (W_3 - W_2)}$$

where D is the density of the water. If water cannot, from the nature of the powder, be employed, any suitable liquid of known density can of course be used, the corresponding value of D being employed in the above formula. Air bubbles must be removed from the powder when in the water or other liquid, and this can generally be achieved by placing the specific gravity bottle and its contents under the receiver of an air pump. A few strokes generally suffice for the removal of any entrapped air.

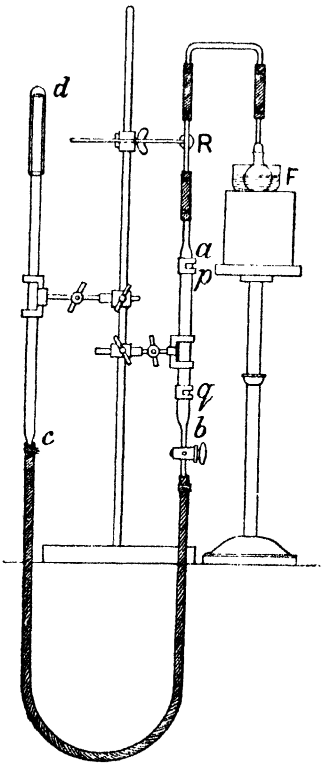


FIG. 72.

In the case of solids which must not be wetted by liquids, or which are porous, the specific gravity is most generally ascertained by means of the volumenometer. This apparatus has taken various forms, but all are based on the same principle.[1] Essentially the method consists in determining the change in pressure accompanying a known change in volume when (1) the original volume contains air only, and (2) when the original volume is partly occupied by the body in question. Bremer's volumenometer is shown in Fig. 72. The wide-mouthed flask F immersed in a water bath is connected by the three-way stopcock R with the tubes *ab* and *cd* containing mercury. On *ab* there are two marks or movable rings at *p* and *q*, and the volume *v* included between these two marks is accurately known. The stopcock R being turned so as to connect both F and *ab* with the air, the tube *cd* is adjusted until the mercury meniscus is at *p*.

[1] Bremer, *Rec. trav. chim.*, 1898, 17, 263; Zehnder, *Ann. Physik*, 1903, 10, 40.

The stopcock R is then turned so as to leave F and *ab* in connection, but shut off from the air. The tube *cd* is then lowered until the top of the mercury meniscus in *ab* is at *q* and the difference of level *h* between the mercury in the two tubes determined, preferably with a cathetometer. A similar operation is carried out when F contains a weighed quantity of the substance being examined, the difference in level now being found to be H^1.

An application of Boyle's Law enables the volume of the body to be calculated from the observed differences of pressure, the atmospheric pressure and the known volume of expansion.

Thus let:—

P = Atmospheric pressure.
V = The original volume under pressure P.
$V+v$ = The final volume under pressure $P-h$.
x = Volume of the body introduced.
$P-h^1$ = The final pressure after expansion in second case.

Applying Boyle's Law:—

$$PV = (P-h)(V+v) \quad . \quad . \quad . \quad (1)$$
$$P(V-x) = (P-h^1)(V-x+v) \quad . \quad . \quad (2)$$

Expansion of (1) and (2) gives after a little transformation

$$x = Pv\frac{h^1-h}{hh^1}.$$

The method is of very general application and gives results easily correct to 1 per cent.

An apparatus resembling the Mohr-Westphal balance has been applied to the determination of the specific gravity of solids.[2] The displacement of the body along the extended beam of a balance, so that the body when weighed in water or other suitable liquid may counterpoise the same tare as when weighed in air in the ordinary position, enables the specific gravity of the body to be ascertained, and furthermore the beam can be divided so as to indicate the specific gravity of the body directly with an accuracy of about 1 per cent.

THE MEASUREMENT OF TEMPERATURE

In chemical technology, the measurement of temperature is an operation of paramount importance. Various means are to hand for the determination of temperature in any given case, such means including, among many others, the ordinary mercury-in-glass thermometer, the platinum resistance thermometer, the thermo-electric pyrometer, and the optical pyrometer.

[2] Gasnault, *J. Physique*, 1916, **6**, 291.

Considering the numerous physical properties which may be, and are made the basis of rational scales of temperature, there is no *a priori* reason existing why temperatures indicated by the same number of degrees on the various scales should represent one and the same temperature. Lord Kelvin has shown that it is possible to construct an absolute thermodynamic scale of temperature—absolute in the sense that its indications are the same whatever the substance which may be chosen as the thermometric body. This absolute scale of temperature is most closely realised in practice by the gas thermometer—preferably containing hydrogen. The departure of the constant-pressure hydrogen gas thermometer from the thermodynamic scale is $+0{\cdot}26°$ at $-200°$ and $0{\cdot}01°$ at $1000°$. The departure is still less in the case of the constant-volume hydrogen thermometer. The gas thermometer allows, therefore, of the realisation in practical form of an absolute scale of temperature, and wherever possible the readings of temperature in technological practice should be referred to this gas scale. The National Physical Laboratory undertakes the calibration of all types of thermometers and pyrometers of sufficiently good construction, and the determination of the correction necessary to convert their readings to the gas scale. It is desirable that every technological laboratory should possess at least one thermometer (or pyrometer as the case may be) which has been so standardised, and the various thermometers employed may then be themselves compared with such standard, the standard itself being sent for re-standardisation at intervals. This method is much to be preferred to the practice of correcting the readings of thermometers and pyrometers by the determination of certain prescribed fixed points such as the melting-point of sulphur under standard conditions. Occasion may, however, arise when the latter course has to be followed, and the following table contains a list of substances suitable for this purpose. All boiling-points as given are determined under a standard atmospheric pressure of 760 mm. of mercury.

Realisation of a Standard Thermodynamic Scale of Temperatures.

Substance.	Transformation.	Temperature (°C.)
Hydrogen	Boiling	$-252{\cdot}7 \pm{\cdot}2$
Oxygen	Boiling	$-182{\cdot}9 \pm{\cdot}1$
Carbon dioxide	Sublimation of solid CO_2 in petrol	$-78{\cdot}5 \pm{\cdot}1$
Mercury	Solidification	$-38{\cdot}88 \pm{\cdot}1$
Ice	Melting	0·0
Phenol	Melting	42·7
Water	Boiling	100·0
Naphthalene	Boiling	218·0
Tin	Freezing	231·8

Substance.	Transformation.	Temperature (°C.)
Glycerol	Boiling	290·0
Benzophenone	Boiling	305·9
Cadmium	Freezing	320·9
Lead	Freezing	327·0
Mercury	Boiling	356·7
Zinc	Freezing	419·4
Sulphur	Boiling	444·5
Antimony	Freezing	630·0
Aluminium	Freezing	657·0
Sodium chloride	Melting	801·0
Silver	Freezing	961·0
Gold	Freezing	1063·0
Copper	Freezing	1083·0
Lithium metasilicate	Freezing	1201·0
Eutectic of nickel and graphite	Freezing	1330·0
Diopside	Melting	1390·0
Lead	Boiling	1525·0
Palladium	Freezing	1549·0
Platinum	Melting	1755·0
Silver	Boiling	1955·0

THERMOMETERS

For purposes of convenience, it is customary to restrict the term "thermometry" to the measurement of temperatures which may be measured by means of a mercury thermometer, the term "pyrometry" being reserved for the measurement of higher temperatures. With ordinary mercury-in-glass thermometers the limit of temperature that can be measured is 300°. With a mercury-in-glass thermometer, the upper space of which is filled with nitrogen or carbon dioxide under 20 atmospheres pressure, and the glass of which is suitably selected, measurements up to 500° are possible. Borosilicate glass 59‴ is generally employed in the construction of such high range thermometers. There is usually an auxiliary bulb at the top, the volume of the bulb being about twenty times that of the internal volume reckoned from 0°. If the thermometer is sealed with the enclosed gas at a pressure of 60 atmospheres, a maximum temperature of 750° may be measured by means of the mercury thermometer.

It is not intended to discuss the various errors to which a mercury thermometer is subject. For these, reference must be made to the works enumerated in the bibliography (p. 227). Many of the corrections and errors are eliminated by having the thermometer calibrated under the conditions of use—*i.e.*, with same stem immersion and same inclination of the thermometer to the vertical. Errors due to the secular variation of the zero are not eliminated in this manner, but are minimised by calibration repeated at frequent intervals. In technical practice, there is generally no necessity for the application

of the various corrections in question. The correction for stem exposure is one, however, that should in general be applied. The magnitude of this correction is generally calculated by the formula:—

$$\text{Correction} = n \times 0.00016(T - t)^\circ$$

where n = Number of degrees in emergent column.
T = Temperature of bath.
t = Temperature of air.

Taking the case of an emergent column of 200°, the bath temperature being 300° and the air temperature 15°, the emergent column correction is:—

$$200 \times .00016 \times 285^\circ = 9.12^\circ.$$

Under such conditions, therefore, the correction for stem exposure is seen to be a large one, and it is well in technical practice to determine the magnitude of the correction in any given case.

In technological work, mercurial thermometers of a robust type are often called for. Thermometers with bulb and stem inclined to one another at various angles are often required, and frequently readings of temperature have to be made under conditions which necessitate the scale being placed at some very considerable distance from the bulb. The bulb and tube are often protected by a sheath. Such sheaths enclosing the bulb should be of as light construction as is compatible with considerations of strength. If a perforated metal tube or other similar arrangement is used for this purpose, the thermometer will indicate the temperature fairly accurately. If an unperforated sheath has to be used, the readings are always too low, even if the sheath is filled up with mercury, copper dust, etc., as should always be done. A wooden handle may be fitted to the thermometer for convenience of handling. Some mechanical protection is afforded by wrapping asbestos round the exposed portions of the thermometer, but the sensitiveness is thereby diminished.

In order to ascertain that the temperature to be measured is not too high for the use of a mercury thermometer, a very practical suggestion due to Weinhold[1] is to place a piece of lead at the spot where the temperature measure is to be made; the melting-point of lead is 327°, and if the test-piece does not show any softening at the edges, even after some time, a mercury thermometer can be safely used.

Hohmann and Maurer have introduced a robust type of mercurial thermometer[2] possessing the advantages that the indicating instrument can, if necessary, be set up at a considerable distance from the point at which the temperature is being determined, and

[1] *Chem. Zeit.*, 1903, **27**, 54.
[2] Supplied by the Cambridge and Paul Scientific Instrument Co.

that furthermore the instrument can be made recording. The principle of this instrument is illustrated in Fig. 73. A is a steel bulb connected by means of a steel capillary B to a special form of steel Bourdon spiral C. The whole system is filled with mercury, and changes of temperature of the bulb give rise to corresponding rises of pressure in the system, which changes of pressure are magnified and may be either indicated by a pointer or recorded by a simple pen mechanism. The record of temperature can be obtained on a chart rotating about its centre at any specified rate. The thermometer being practically wholly metallic, there is considerable

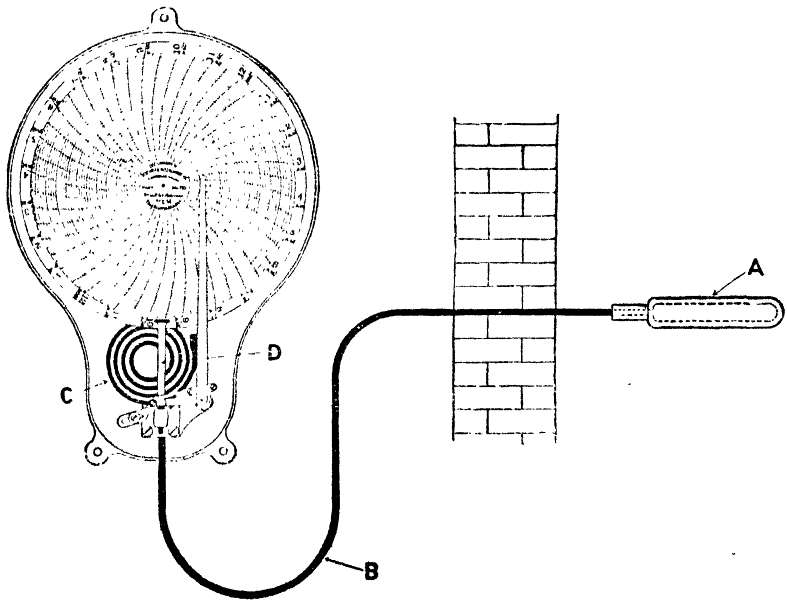


FIG. 73.

conduction along the stem from the heated bulb, and the principal error in such instruments arises from such conduction and from stem exposure. The thermometer should be calibrated under conditions reproducing as nearly as possible the conditions of use. The instruments are capable of recording temperatures up to 540° with an accuracy of about 1 per cent. Two independent records of temperature can be obtained on the same chart, such temperatures approaching to within 5° of each other, but not overlapping. Such an arrangement is particularly applicable to cases such as the recording of temperatures of inlet and outlet-feed water, etc. The indicating and recording instruments can be enclosed, and may be fitted with an alarm arrangement indicating the attainment of maximum or minimum temperatures.

PYROMETERS

1. Platinum Resistance Thermometers.

For temperatures above those for which the mercury-in-glass thermometer may be employed, recourse may be had to thermometric devices of very varying types. Some of these are also capable of use within the range of the mercurial thermometer, but find their most general application at the higher ranges of temperature. The most accurate form of pyrometer is undoubtedly the platinum resistance thermometer. The method of determining temperature by ascertaining the resistance of a platinum wire wound on a pipe-clay cylinder and enclosed in a tube of wrought iron was introduced by Siemens in 1871. The device was found unsatisfactory by a Committee of the British Association, and the source of trouble was traced to combination between the platinum and silicon produced by reduction of the material of the pipe-clay in the reducing atmosphere produced by the highly-heated casing. H. L. Callendar[1] devised a form of platinum resistance thermometer from which all the inconsistencies of the Siemens instrument were absent; and by his work and his joint work with E. H. Griffiths[2] has established a system of practical pyrometry of extreme precision. Temperature indicated by a platinum thermometer is generally represented by "pt" and is defined by the relation:—

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where R_{100} is the resistance of the platinum wire at 100°,
R_0 is the resistance of the platinum wire at 0°,
and R is the resistance of the platinum wire at the temperature pt on the scale of the platinum thermometer, or $t°$.

The relation (i.) above defines the scale of the platinum resistance thermometer. As already pointed out, there is no *a priori* reason why the platinum scale of temperature so defined should agree with the scale defined by the gas thermometer. Callendar showed that the relation between R_t and the temperature measured by the gas thermometer can be represented by a parabolic formula of the type:—

$$R_t = R_0 (1 + \alpha t + \beta t^2) \quad . \quad . \quad . \quad \text{(ii.)}$$

From (ii.) it follows at once that the relation between t and pt is of the form:—

$$t - pt = \delta \left\{ \left(\frac{t}{100} \right) - \frac{t}{100} \right\} \quad . \quad . \quad . \quad \text{(iii.)}$$

[1] *Phil. Trans.*, A., 1887, **178**, 160; *Phil. Mag.*, 1891 [v.], **32**, 104; *Phil. Mag.*, 1899 [v.], **47**, 191, 519.
[2] *Phil. Trans.*, A., 1892, **182**, 43, 119.

δ is termed the difference co-efficient of the sample of wire employed, and its numerical value for pure platinum is 1·5. Its value in any given case is obtained by ascertaining the boiling-point of sulphur by means of the thermometer in question. It is obvious from this relation that, in general, the value attributed to a given temperature on the platinum scale is not identical with the value attributed to it on the gas scale, which is to be regarded as the standard scale of temperature. As is shown by (iii.), and indeed as must necessarily be the case by definition, the scales agree at 0° and 100°, but at all other temperatures differences exist in the values attributed to one and the same temperature measured on the two scales. Thus at 1000° for a platinum thermometer having $\delta = 1 \cdot 5$

$$t - pt = 1.5\left\{\left(\frac{1000}{100}\right)^2 - \frac{1000}{100}\right\} = 135^\circ.$$

The possible differences between the two scales are therefore seen to be by no means inconsiderable. In technological practice, however, the necessity for the correction of the platinum scale to the scale of the gas thermometer seldom if ever arises, as the indicating or recording instrument used with the platinum thermometer is almost invariably graduated in terms of the latter scale.

Essentially, the platinum resistance thermometer consists of a coil of fine platinum wire wound on a mica frame and attached to terminals so that the resistance of the coil can be ascertained when the coil is exposed to any given temperature, and the measure of such resistance serves as an indication of the temperature to which the coil of wire is exposed. The resistance coil is inserted in one arm of a Wheatstone bridge, the ratio arms of which are adjusted to equality, and the value of the resistance in the opposite arm of the bridge required to produce balance of the bridge, as indicated by a galvanometer, determined. The error due to stem exposure, which is inherent in practically all other forms of pyrometer, can be entirely and accurately eliminated by the use of a pair of "compensating leads" inserted in the arm of the bridge opposite to the arm in which the coil of platinum wire is inserted, these leads lying everywhere alongside the leads from the platinum coil.

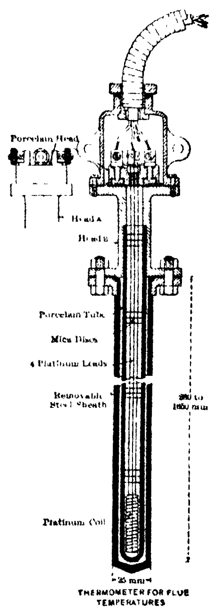


FIG. 74.

A form of platinum thermometer suitable for industrial use is illustrated in Fig. 74. The platinum coil is shown protected by a removable steel sheath and surrounded by a robust porcelain tube.

Alternatively, the coil may be enclosed in a porcelain or silica sheath and the whole surrounded by a steel or fire-clay sheath. The terminals are enclosed in a porcelain or aluminium head. The thermometer can also be provided with a suspension device attached to the head, the device being useful for insertion of the pyrometer in salt-bath furnaces, etc. By means of leads, the pyrometer is connected with the indicating or recording instrument. Four-way copper leads are generally employed. These are inserted in opposite arms of the bridge as already described, and variations in their resistances due to changes of temperature are therefore automatically eliminated. In some cases it is convenient to run a few feet of armoured leads from the pyrometer head to a

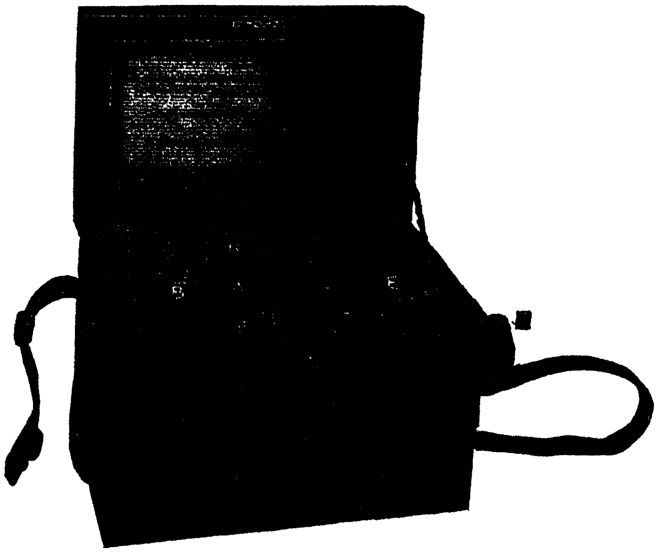


FIG. 75.

junction box and then to continue therefrom to the indicator or recorder by means of flexible, braided or lead-covered cables.

Many adaptations of the Wheatstone bridge have been made for purposes of determining and indicating temperature by means of a platinum resistance thermometer. For scientific investigations of extreme accuracy, the methods devised by Callendar and Griffiths, Leeds and Northrup, may be mentioned. For industrial purposes the following methods amongst others are available.

The Whipple Indicator[1] (Fig. 75) is a form of Wheatstone bridge in which a balance of the bridge is obtained by turning the handle, H; the instrument is calibrated to give direct readings of temperature. The galvanometer and the coils constituting the arms of the bridge are contained inside the case, and the necessary current is supplied

[1] Supplied by the Cambridge and Paul Scientific Instrument Co.

by two small dry cells, E, these cells only requiring renewal after long intervals. The indicator is connected to the resistance thermometer by 4-way leads which may be of any desired length, the stem exposure correction being automatically eliminated as already explained. When taking a reading, the key, F, is pressed, and the movement of the pointer beneath the window, A, observed. By turning H in the appropriate direction, the balance of the bridge is restored, the resistances included in two arms of the bridge being varied by the turning of H. When balance of the bridge is obtained, as evidenced by the pointer regaining its zero position, the temperature is read off directly from the scale in the window. The scale of the indicator is an extremely open one, the total length being about 18 ft. with a range from $-10°$ to $1200°$, the average length of $1°$ being a fifth of an inch. The instrument can be used as a standard pyrometer for the calibration of works instruments.

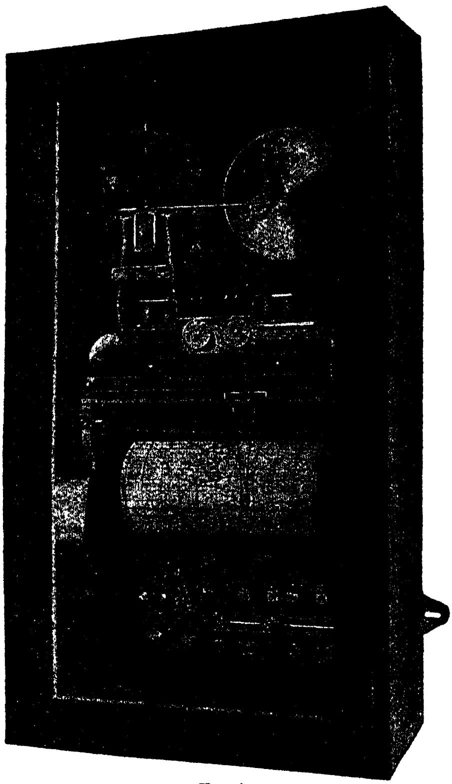


FIG. 76.

The Callendar Recorder[1] (Fig. 76) utilises the principle of the Wheatstone bridge, the balancing being achieved automatically. The pen arm is attached to the contact which slides to and fro on the bridge wire. The movement of the pen is controlled by a clock, which is itself controlled by two electromagnets. Two insulated wires are attached to the galvanometer pointer, and the wires make contact on one side or the other of a platinum-rimmed contact wheel. When correct registration is indicated, these wires are out of contact with the wheel. When the bridge is upset by an alteration in temperature of the platinum resistance coil, contact is made between the wheel and one or other of the wires, one of the electromagnets is energised and the clock released. The balanced condition of the bridge is restored by movement of the pen arms along the bridge wire, and the two wires are once more out of contact with the wheel. The

[1] Supplied by the Cambridge and Paul Scientific Instrument Co.

necessary current for operation of the bridge is provided by a 4-volt accumulator. Continuous records over various periods of hours or days are possible with the recorder, and various ranges of temperature between 0° and 1000° can be very accurately recorded.

The Leeds and Northrup Indicators, of various types, utilise either the differential galvanometer or the Kelvin double bridge. In a type of instrument with adjustable scale, the instrument may be set to any desired temperature, and the variation of temperature from such desired temperature is indicated by the motion of a pointer to left or right of zero, the amount of departure from the desired temperature being directly indicated. The instrument can, if desired, be run from an ordinary lighting circuit, and a departure of 2° from the set temperature is quickly readable by the workman.

Other instruments indicating temperature and employing platinum resistance thermometers have been introduced by R. W. Paul, employing the principle of the two-coil ohmmeter, and by Messrs Carpentier and Joly. Details of these instruments will be found in *Measurement of High Temperatures* by Burgess and Le Chatelier. The mounting of resistance thermometers will be referred to later.

2. Thermo-Electric Pyrometers.

The thermo-electric pyrometer had its origin in the discovery of Seebeck in 1830, that the junction of two metals heated to any temperature is the seat of an electromotive force. The magnitude of the electromotive force depends upon the nature of the metals forming the junction, and is a function of the difference of temperature between the hot junction and other junctions in the circuit. The electromotive force is furthermore largely dependent upon the state of purity of the respective metals constituting the junction. In general, if a circuit be made of two metals A and B, the metal A being employed for completing the circuit in which is included a galvanometer as indicating instrument, then if one junction of A and B is maintained at a temperature $t°$, while the remaining junction of A and B is maintained at a different temperature, the galvanometer will indicate that an E.M.F. is developed in the circuit, and that the magnitude of such E.M.F. depends upon the difference of temperature between the hot and cold junctions. It is found that a suitable form of relation between the E.M.F. and the temperature difference is furnished by the expression:—

$$E_t = a + bt + ct^2$$

where a, b, and c are constants, and E_t represents the value of the E.M.F. developed in the circuit when a difference of temperature equal to $t°$ is established between the hot and cold junctions. The magnitude

of the E.M.F. developed in the circuit is in any case small, and remarkable variations are shown in the magnitude of the E.M.F. generated by couples composed of different pairs of metal when subjected to the same temperature difference between the hot and cold junctions. Thus a copper-constantan couple gives an E.M.F. of the order of 50 microvolts per degree up to 300°, whereas for a platinum, platinum—10 per cent. rhodium couple the E.M.F. developed is of the order of 0·6 microvolt per degree over the same range. With a couple composed of copper and iron, the E.M.F. developed for a similar difference of temperature would be of the order 0·01 volt.

The most accurate method by which the magnitude of the E.M.F. generated in any case can be determined is undoubtedly by means of the potentiometer. In technical work, however, the usual practice is to form a closed circuit of the thermocouple, a galvanometer and the leads joining the couple to the galvanometer. The E.M.F. generated in the circuit when a difference of temperature is established between the two junctions generates a current in the circuit, and this current produces a deflection of the galvanometer, the pointer moving over a scale which has been empirically graduated to denote the temperature to which the hot junction is heated, the cold junction being maintained throughout at the temperature for which the galvanometer was calibrated.

With regard to the material constituting the thermocouple, a wide choice is available. Undoubtedly the most reliable couples are those formed of the noble metals, platinum, iridium, and rhodium, and alloys of the same. Contrasted with thermocouples composed of the base metals such as nickel, copper, iron, the couples composed of the metals of the platinum group possess the advantage of far greater reliability and an extended range of temperature over which they may be employed. The base-metal couples, however, are not without compensating advantages, such as cheapness, so that couples of thick wires and consequent low resistance can be employed, robustness in use, and the greater magnitude of the E.M.F. developed for a given difference of temperature compared with the corresponding E.M.F. in the case of the noble groups of metals and alloys.

The following is the scheme recommended by E. Griffiths,[1] as indicating suitable materials for couples to be employed up to various maximum temperatures :—

Maximum Temperature.	Thermocouple.
300° . .	Iron-constantan.
600° . .	Iron-nickel.
1200° . .	Alloy of copper-nickel and alloy of chromium-nickel.
1600° . .	Platinum and alloy of platinum with 10 per cent. rhodium.

The maximum temperature, 1600° indicated above, is probably outside

[1] *Methods of Measuring Temperature*, 1918, p. 59.

the limit of use in an industrial installation, and it is recommended that the platinum—platinum-rhodium couple be not used above 1400°, care being taken that the couple when employed at temperatures above 1000° is shielded from metallic vapours, reducing gases, and carbonaceous matter.

The couple should be protected by either quartz or porcelain, and for permanent installations the pyrometer should be further protected by insertion in a sheath of steel or fire-clay. Base-metal couples are sometimes exposed without protection, under various conditions, to high temperatures. They should then receive frequent calibration. Instead of such a protecting sheath of steel or fire-clay, which is suitable for large furnaces, other protecting devices can be readily made, adapted for use with crucibles, tubes, and other laboratory forms of apparatus. One of the great advantages of the instrument is that it can be used equally well for the measurement of the temperature of either large or small masses of material, as the junction of the constituent metals or alloys alone requires to be exposed to the temperature to be measured.

The "cold" junction should, wherever possible, be maintained at the temperature for which the indicator was calibrated. This may be achieved by immersing the junction in ice, or having a water-cooled junction. Where this is impossible it may be desirable to bury the cold junction in the earth under the roof of a building and as near the centre of the floor as possible, as recommended by Whipple.[1] The junction is immersed to a depth of 10 ft. or more if possible. Under such conditions, in an industrial installation, the variation of the temperature of the cold junction has been found to be no more than 1·5° for a period of six months. In the case of an installation where such a procedure is impossible, compensating leads,[2] of copper or cupro-nickel respectively, may be employed in the case of couples composed of metals or alloys of the platinum group, whereby the cold junction is transferred to a position of known temperature such as the indicator or recorder. Failing any of these devices, the adjustment of the zero of the indicator is made to the temperature of the cold junction as indicated by a thermometer, prior to taking a reading. For this purpose the couple is disconnected, the adjustment made, then the circuit completed once more and the temperature observed. Attempts have been made to eliminate automatically the cold junction correction. Thus, in Bristol's compensator, a small bulb containing mercury, and with a narrow neck, is inserted in the thermoelectric circuit close to the cold junction. A short loop of platinum wire forming part of the circuit dips in the mercury. A rise of

[1] *Pyrometers and Pyrometry*, Faraday Soc. Publication, 1917, p. 51.
[2] *B. P.*, 1909, No. 370; *Proc. Inst. Mech. Eng.*, 1913, p. 729.

temperature of the bulb is accompanied by an expansion of the mercury in the bulb, thus cutting out a little of the platinum wire from the circuit, an effect which can be made to counterbalance the effect of the diminished E.M.F. due to increase of temperature of the "cold" junction. Multiple scale instruments provided with various scales to be employed for different cold junction temperatures, all being engraved on one card, are also available.

Care should be taken in connecting the thermocouple to the indicating or recording instrument. In addition to the Seebeck effect responsible for the E.M.F. when one junction is at a higher temperature than another in the circuit, another thermo-electric effect may enter into consideration unless care is exercised. A *homogeneous* wire heated in different parts to different temperatures may itself be the seat of E.M.F. The existence of this phenomenon necessitates the leads being set up in pairs lying contiguously to one another, so that any possible effect of this nature in one lead is counterbalanced by a similar E.M.F. in the opposite direction in the other lead. The leads should be protected by metal sheathing, or, if necessary, water jacketed. When exposed to high temperature, the wire from the hot junction should be protected by means of asbestos or pipe stems. With asbestos a temperature up to 1300° can be measured; above this temperature, asbestos melts. Hard porcelain can be employed up to 1500°, and so-called "Marquardt mixture" up to 1600°.

With regard to indicating or recording instruments, it has already been pointed out that the E.M.F., even in the case of a base-metal couple, is very small. The potentiometer is practically never employed in technical practice for several reasons, the chief being that the method is a null one, and hence does not permit of temperatures being read at sight; "Deflection" potentiometers are, however, available. In customary technological practice, a galvanometer, generally of the moving coil type, is invariably used. The resistance of the galvanometer should be high compared with that of the couple with which it is employed. It is possible to use thick wires of base metals of consequently low resistance, so that a galvanometer of lower resistance than with couples of the noble metals may be employed. The galvanometer base metal may be of a more robust kind, consequent on the increased E.M.F. generated with the couples. The zero of the indicator should be adjustable by means of a screw or other device. The casing should render the indications of the instrument unaffected by any external magnetic field, and should be dust-proof. The coil of the galvanometer should preferably be wound with wire of low temperature co-efficient, such as manganin.

Recording instruments for use with thermocouples must of necessity be of delicate construction. The magnitude of the E.M.F. being small,

friction of the parts of the recording device may interfere very considerably with the record. For this reason, in most recording devices for use with thermocouples, the record is of an intermittent character. The recording pen is in general raised out of contact with the paper for the greater part of the time during which a record is required, and only makes contact for a short space of time when depressed by suitable mechanism, being free in the meantime to take up a new position determined by the temperature to which the hot junction of the thermocouple is exposed. The record is then obtained in the form of a series of dots which are so near together as to form practically a continuous line.

The Thread Recorder mentioned on page 133, and supplied by the Cambridge and Paul Scientific Instrument Co., is employed in this manner, the pointer of a moving coil galvanometer depressing an inked thread upon a moving chart at intervals determined by clockwork. An indicating or recording device may, by the use of a suitable switch, be employed with any number of thermocouples. Such switches must be free from bad contacts. With base-metal couples, a low resistance indicator being generally employed, errors due to such contacts may be extremely large.

The thermocouple, suitably chosen and installed, may be employed over the range from 300° to 1600° with an accuracy of about 5° throughout the range. The following table indicates instruments which should be used over the ranges of temperature specified, and the accuracy attainable with an industrial installation :—

Range.	Instrument.	Accuracy Attainable.
0 to 900°	Platinum resistance thermometer	1°.
0 „ 600°	Iron-constantan or copper-constantan couple	5°.
0 „ 1600°	Platinum—platinum-rhodium couple	5°.

The indications of thermo-electric and other types of pyrometers should be verified from time to time by submission to the National Physical Laboratory, or by comparison with an instrument of similar type whose calibration has recently been carried out at that laboratory.

With regard to the installation of pyrometric appliances, care should be taken that, wherever possible, the pyrometer of whatever kind, is inserted so as to lie along an isothermal, *i.e.*, so that no difference of temperature exists between different parts of the pyrometer. Where this is not possible—and it must be recognised that in most cases it is not possible—the pyrometer should be installed with the minimum departure from the requirement. Variations of temperature along the pyrometer are accompanied by conduction of heat along the pyrometer substance, and on this account the indication of the instrument

employed will not be that corresponding to the temperature at the place where the thermo-junction or other device is situate, but will be conditioned partly by such heat conduction. The error from this cause may in certain circumstances be of large amount.

3. Radiation Pyrometers.

For practical purposes, three methods of application of the laws of radiation are available for the purpose of determining temperatures :—

1. By measurement of the total intensity of the radiation, and the application of the Stefan-Boltzmann law, connecting the radiation from a black body with its temperature and that of its surroundings, in the form $S = \sigma\ (\theta^4 - \theta^4_0)$ where θ is the temperature of the body, θ_0 that of the surroundings.
2. By measurement of the intensity of the radiation of a definite wave length and the application of Wien's law, connecting relations between the spectrum constituents of radiation with the temperature of the radiating body.
3. By measurement of the relative intensity of the radiation of definite wave lengths and the application of Wien's law.

The following are some applications of these methods which are available for technological purposes :—

(1) Total Radiation Pyrometers.

Féry's pyrometer, supplied by the Cambridge and Paul Scientific Instrument Co., is shown diagrammatically in Fig. 77. Essentially, this consists of a delicate thermocouple, S, upon which the radiation is

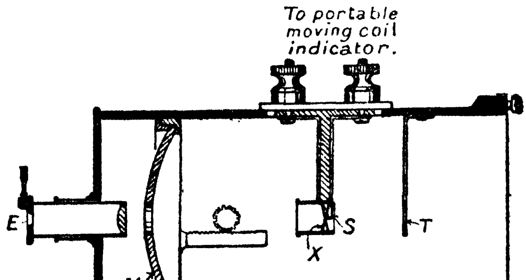


FIG. 77.

focussed by means of the mirror, M. The tongue, T, shields the cold junction of the couple, which is further protected by a box surrounding the couple and the inclined mirrors, X. The observer's eye is placed

at E, and the wide end of the instrument directed towards the source of radiation, such as the interior of a retort setting. The instrument is first focussed so that the radiation falls accurately on the hot junction. This is achieved by racking the mirror M backwards or forwards until the image of a straight line seen through E is exactly in the plane of the inclined mirrors previously mentioned. When this is the case, there is no relative displacement of the two images of the line as seen in the two halves of the eye-piece. This adjustment is one that can be readily achieved. The couple is connected with a galvanometer, and the readings of this instrument indicate the temperature of the radiation to which the instrument is directed. The instrument can also be connected with a recording device. In order to reduce absorption of heat by the material of the mirror, this is frequently made of glass, coated on its front surface with gold or nickel.

A modified form of this instrument, also supplied by the Cambridge and Paul Scientific Instrument Co., employs a spiral spring in place of a thermocouple. The spring is bi-metallic, and is rolled very thin and coiled into a very small spiral (about $\frac{1}{8}$ in. in diameter and $\frac{5}{64}$ in. deep). The centre of the spiral is fixed, and the free end carries a light aluminium pointer which, with alterations in temperature of the spring, moves over a graduated dial. The dial is empirically graduated, so that the indications of the pointer denote the temperature of the body on which the instrument is sighted.

With the thermocouple type of Féry instrument, the object sighted on must be at least 1 ft. in diameter for every 2 ft. distance between the telescope and object, while with the spiral type, the object must be at least 1 in. in diameter for every 18 in. of such distance. These conditions being satisfied, the indications are independent of distance. The range of temperature that can be measured with a series of these instruments is from 500° to 1700°. The scale of such instruments is sometimes extended by the use of a diaphragm and second scale.

The necessity for accurate focussing is obviated in the Foster fixed-focus type of pyrometer supplied by the Foster Instrument Co., Letchworth, this result being achieved by locating the front diaphragm of the instrument and the receiving disc of the couple at conjugate foci of the mirror which reflects the radiation on to the disc of the thermocouple. This instrument requires a rather larger area for sighting purposes than instruments of the variable focus type. It can be obtained in either the indicating or the recording form. A similar instrument has been introduced by Thwing,[1] employing a reflecting cone in place of a concave mirror. In a modification due to Whipple, a salamander or fire-clay tube is introduced into

[1] *Phys. Rev.*, 1908, 26, 190.

the heated enclosure, and the radiation from the hot-end of the tube received on a delicate thermocouple.

The precautions necessary to be taken in the use of the instruments described have been well summarised by E. Griffiths.[1]

(2) Optical Pyrometers.

The theoretical basis of the total radiation pyrometers described above has been more firmly established than that of the optical pyrometers dependent upon the measurements of the intensity of the radiation of a definite wave length. The latter, however, possess certain advantages, not the least of which consists in the fact that they may be used for ascertaining the temperature of bodies of smaller dimensions than is possible with pyrometers of the former class.

There are two types of this class of instrument. In the one type,

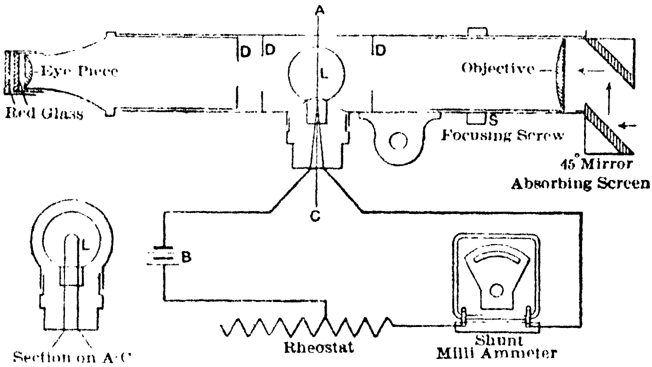


FIG. 78.—Holborn-Kurlbaum Pyrometer.

the temperature of the body upon which the instrument is sighted is ascertained by adjusting the current through an incandescent filament until such filament "disappears" against the background furnished by the radiation from the body upon which the instrument is sighted. The monochromatic illumination, *i.e.*, radiation of definite wave length in such an instrument, is secured by the use of a filter of red glass in the eye-piece of the sighting telescope. Such an instrument was introduced by Morse, and modified by Holborn and Kurlbaum.[2] The instrument is illustrated in Fig. 78. The instrument is calibrated by sighting upon an electric furnace, the temperature of which is simultaneously measured by a thermocouple. Ordinarily, the instrument can be used up to a temperature of 1400°, and by the use of an absorption screen consisting of two black glass mirrors, inclined at 45°, the range is extended to 2700°. Various other types

[1] *Methods of Measuring Temperature*, 1918, p. 93.

[2] *Ann. Physik*, 1902, 10, 225.

of absorbing screens are similarly employed. The use of a spectroscopic eye-piece, as introduced by Mendenhall,[1] increases the accuracy of the instrument.

In other types of optical pyrometer, the radiation from the heated body and the radiation from an incandescent filament are compared, the application of Wien's law being justified by the simultaneous isolation of radiation comprised within a narrow range of wave lengths from each beam. The best known instrument of this class is the Wanner pyrometer, manufactured by the Cambridge and Paul Scientific Instrument Co. Briefly, the principle of the instrument is as follows: — Light from the object whose temperature is to be

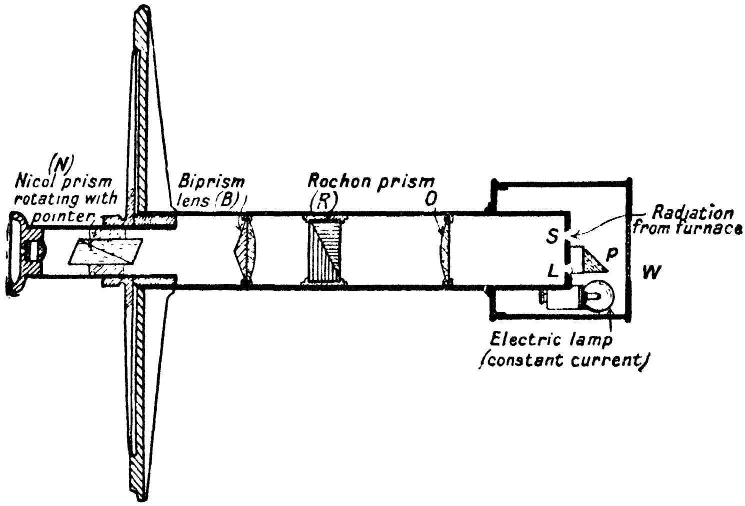


FIG. 79.

measured, and light from an electric lamp supplied with constant current, pass respectively through the two halves of the telescopic arrangement shown in Fig. 79. These beams pass through the system of lenses and prisms shown. The two beams are polarised in different planes on passing through the Rochon prism and are rendered monochromatic. Finally the two beams pass through a single eye-piece, and the field of view is divided into two semi-circular halves separately illuminated by the two beams. In general, the intensity of illumination of the two halves of the field is different, but adjustment to equality is effected by rotating the eye-piece, containing a Nicol prism, to which a pointer is attached, the reading of the pointer indicating directly the temperature of the body on which the pyrometer is sighted. The current supplied to the electric lamp is maintained at a constant pre-determined value by means of a rheostat, the value

[1] *Phys. Rev.*, 1911, **33**, 74.

being read on an ammeter. As occasion arises, the electric lamp is standardised against an amyl-acetate lamp, the value of the current necessary for adjustment to equality of illumination of the two halves of the field of vision in this case being that employed in subsequent use in the instrument. The range of employment of the instrument is ordinarily from just below 700° to 1400°. By the use of absorption screens, the scale may be adjusted to the following ranges:—900°-2000°, 1200°-2500°, and 1400°-4000°.

Amongst other optical pyrometers may be mentioned the Shore pyroscope, the Féry absorption pyrometer, and the Burgess pyrometer for determining melting-points of microscopic samples. Allied to instruments of this class are optical pyrometers, such as the Wedge pyrometer, the Stereo pyrometer, and the pyromike, readings taken with which are affected to some extent by the acuity of vision of the observer, but which, used with caution, are capable of affording much useful information in technical practice.

Seger Cones

The method of employing a series of mixtures of vitreous materials to establish a scale of temperature was originally conceived by Lauth and Vogt about 1880. The method was much developed by Seger, and further extended by Cramer and Hecht.[1] The temperature scale in the original form devised by Seger has been modified and extended by later practice, and the following table is the present-day designation of the various cones and their respective squatting temperatures:—

Squatting Temperatures of Seger Cones.

Cone No.	°C.	°F.	Cone No.	°C.	°F.	Cone No.	°C.	°F.	Cone No.	°C.	°F.
022	600	1112	07A	960	1760	9	1280	2336	29	1650	3002
021	650	1202	06A	980	1796	10	1300	2372	30	1670	3038
020	670	1238	05A	1000	1832	11	1320	2408	31	1690	3074
019	690	1274	04A	1020	1868	12	1350	2462	32	1710	3110
018	710	1310	03A	1040	1904	13	1380	2516	33	1730	3146
017	730	1346	02A	1060	1940	14	1410	2570	34	1750	3182
016	750	1382	01A	1080	1976	15	1435	2615	35	1770	3218
015A	790	1454	1A	1100	2012	16	1460	2660	36	1790	3254
014A	815	1499	2A	1120	2048	17	1480	2696	37	1825	3317
013A	835	1535	3A	1140	2084	18	1500	2732	38	1850	3362
012A	855	1571	4A	1160	2120	19	1520	2768	39	1880	3416
011A	880	1616	5A	1180	2156	20	1530	2786	40	1920	3488
010A	900	1652	6A	1200	2192	26	1580	2876	41	1960	3560
09A	920	1688	7	1230	2246	27	1610	2930	42	2000	3632
08A	940	1724	8	1250	2282	28	1630	2966			

[1] *Tonindustrie Zeit.*, 1896, No. 18.

In use, a selection of the cones, suitably chosen according to the temperature to be measured, is placed in sequence on a tile so as to be visible from outside the kiln or furnace. The order of fusion is observed, and the temperature taken as that indicated by the cones whose summit bends so as just to touch the tile. The cones are composed of mixtures, in various proportions of pure quartz sand, felspar, kaolin, calcium and magnesium carbonates, boric acid, with a small proportion of iron oxide in some of the cones. The cones should be calibrated under conditions of rate of heating approximating to that to which they will be subjected in practice. With very slow heating the cones may soften at temperatures from 40° to 70° below those indicated in the above table. The squatting temperatures are largely affected by the atmosphere in which the cones are heated.[1] Thus differences of as much as 110° were obtained in the squatting temperature of cones 9 and 10, when heated in the electric furnace and a ceramic kiln respectively, the heating being prolonged over a period of sixty hours. The cones can be used with confidence to give relative temperatures correct to 25° at the higher range, but too great reliance must not be placed upon the absolute temperature indicated by the cones in any given case.

Analogous methods of temperature measurement are furnished by Watkin's recorders, Holdcroft's thermoscopes, and Wengers' calorites.[2] Wiborgh's thermophones consist of an explosive surrounded by a fireproof substance and made up in cartridge form. The time is noted between the time of introduction of the thermophone and the explosion of the cartridge. The times are measured to one-fifth second, and results concordant to 20° are obtainable at 1000°.

Amongst other pyrometers of various types may be mentioned the hot-blast pyrometer, employing the principle of dilution of the hot blast with cold air, Wiborgh's air pyrometer, and the Siemens calorimetric pyrometer. These and various other types of industrial pyrometers are described in *The Measurement of High Temperatures*, by Burgess and Le Chatelier. Various other types, particularly applicable to technological practice, will be found in the Report of the Faraday Society of the discussion held in 1917 on "Pyrometers and Pyrometry."

[1] See Burgess and Le Chatelier, *The Measurement of High Temperatures*, 1912, p. 376.

[2] See *Pottery Materials*, Watkins, in *Pyrometers and Pyrometry*, published by Faraday Society, 1917.

THE MEASUREMENT OF PRESSURE AND OF DRAUGHT

MANOMETERS

The determination of the pressure in a current of gas is often necessary in technical work, especially those relatively small differences of pressure which occur in chimneys, gas generators, sulphuric acid chambers, and the like: indeed many chemical processes can only be rationally conducted with the aid of systematic measurements of this nature. Observations of the differences of pressure registered by the instruments are sometimes sufficient, whilst in other cases the velocity of the current of gas and the quantity of gas flowing in the system are deduced from the observations by calculation.

Instruments which simply measure the statical difference of pressure between the adjacent spaces, usually between the inside of an apparatus and the external atmosphere, are called pressure gauges or manometers. Pressure anemometers are those which measure the difference between the static and dynamic pressures at a point in a stream of fluid. The pressure is read and recorded in a variety of units. Thus it may be expressed in pounds per square inch, in tenths of an inch of water column, in millimetres of mercury, etc. The conversion from one mode of expression to another is often necessary, and is readily carried out by an application of the hydrostatic result that the increase of pressure due to a depth, H of liquid of density ρ is $g\rho H$ absolute units, or is proportional to ρH. Thus, by way of example, a pressure of 760 mm. of mercury

$$
\begin{aligned}
&= 760 \times 13.6 \text{ mm. water} = \frac{760 \times 13.6}{10 \times 2.54 \times 12} \text{ feet of water} \\
&= 33.9 \text{ feet of water} \\
&= \frac{33.9 \times 12 \times 62.3}{1728} \text{ lbs. per sq. in.} \\
&= 14.68 \text{ lbs. per sq. in.}
\end{aligned}
$$

Of the many forms of pressure gauges the simplest consists of a glass U-tube provided with a scale (Fig. 80). When the pressure at any point in a current of gas is to be ascertained, one limb of the tube A is put in communication with that point by means of the tube D, and the other limb B is open to the atmosphere. The pressure at the point in question is then greater or less than the atmospheric pressure by an amount proportional to the difference in level of the

liquid in the two limbs. The question as to whether there is an excess or deficit with regard to the atmospheric pressure is settled by noting whether the level of the liquid in the limb open to the atmosphere is respectively above or below the level in the other limb.

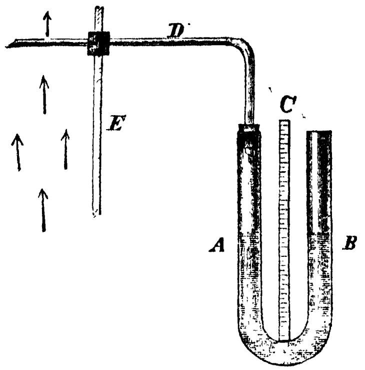


FIG. 80.

In addition to the simple form of U-tube, the hydrostatic gauge has been modified so as to appear as a single tube, the remaining tube taking the form of a wide cylindrical vessel. A float swims on the surface of the liquid in the narrow tube, and is connected with a horizontal indicator by means of a fine string passing over a small pulley.

King's gauge (Fig. 81) is essentially a U-tube modified, so that one limb surrounds the other. A float on the liquid in one limb is connected with a string passing over a pulley wheel, balance of the pulley wheel being maintained by the use of a small weight attached to a string wrapped round the wheel in the opposite direction. The pulley wheel is mounted on friction wheels, and its rotation by change of level of the water is indicated by the motion of a pointer connected to it. The scale is divided, so that readings of pressure correct to $\frac{1}{100}$ in. can readily be made. Such gauges are especially serviceable for the measurement of pressures up to about one foot of water column.

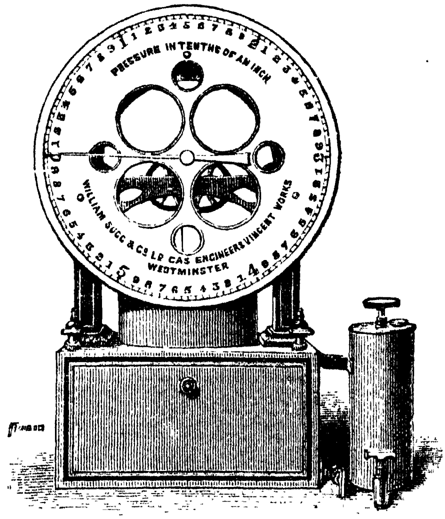


FIG. 81.

The principle of the aneroid has been applied by the Cambridge and Paul Scientific Instrument Co. in a convenient portable pressure gauge for the measurement of gaseous pressures up to about 10 in. of water column (Fig. 82). The zero adjustment is effected by rotating the dial of the instrument, the instrument being meanwhile held in the position in which it is subsequently employed. Such instruments require calibration from time to time, owing to variation in the elastic properties of

the material of the aneroid. Instruments of similar type are available for the measurement of pressures of the order of 100 in. of water.

For the indication of higher pressures, frequently met with in technological practice, instruments of the Bourdon gauge type are generally used. In these a deformation of a sealed steel tube, one end of which is fixed, is produced when the interior of the tube is exposed to pressure, and the motion of the free end of the sealed tube moves a pointer or other device serving to indicate the pressure to which the tube is subjected. Such gauges can be obtained to indicate a pressure of 12,000 lbs. per sq. in., and pressure gauges of special design, such as crusher gauges, are available for the measurement of still higher pressures. Various devices—mechanical and optical—have been introduced for the measurement and recording of the pressures developed by the explosion of gaseous mixtures.[1]

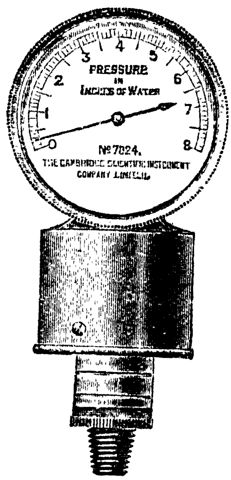


FIG. 82.

Gauges of the types already described can readily be made recording, the indicator or pointer merely being supplied with a receptacle for ink, and its indications recorded on a suitable chart driven by clockwork at an appropriate rate. Such devices can also be obtained with arrangements whereby a bell is rung when any predetermined pressure is exceeded or when the pressure falls below a predetermined figure.

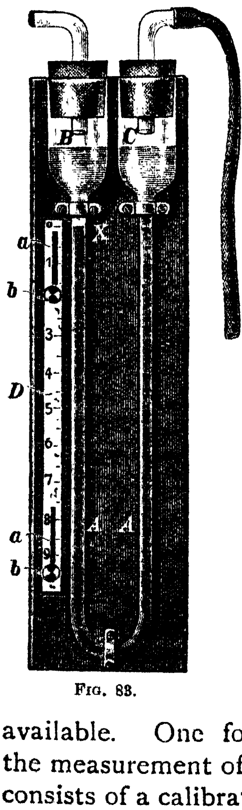


FIG. 83.

In technological practice, it is often necessary to measure minute differences of pressure. The measurement of the draught in a flue necessitates the measurement of a deficit of pressure of the order of 0·1 mm. of water. The accurate measurement of such minute pressure differences necessitates the use of special appliances: various micro-manometers, as they are called, are available. One form of micro-manometer, designed by Seger, for the measurement of draught and of pressure is shown in Fig. 83. This consists of a calibrated glass U-tube, A, both ends of which end in large

[1] *Cf.* Watson, *Proc. Inst. Automobile Engineers*, 1900, p. 391; Wheeler, *J. Chem. Soc.*, 1911, 113, 855.

glass tubes, B and C, of equal diameter. The tube, B, A, C, is fastened to a board which also supports a sliding scale, D, fixed parallel to one limb of A, and adjustable by means of slits *a a* and screw pins *b b*. The U-tube is filled with two non-miscible liquids, having the same specific gravity, in such a manner that their point of contact is near the zero of the scale. Water and aniline, or light petroleum spirit and dilute alcohol, are suitable pairs of liquids for use in the apparatus. B and C being exposed to atmospheric pressure, the point of contact of the two liquids is adjusted to the zero of the scale. When B and C are exposed to pressures differing slightly, a small difference of level of the liquid in the upper wide portions of the two limbs occurs, and the difference is multiplied in the movement of the surface of contact of the liquids in A in the ratio of the sectional areas of B and C to that of the narrow tube A. When the specific gravities of the two liquids are not exactly the same, the necessary formula for the conversion of the motion of the surface of contact to the equivalent difference of pressure in B and C is slightly more complicated, but in any case, the scale can be graduated to indicate such difference of pressure directly.

A modification of the Seger instrument is found in König's differential manometer in which the two limbs are concentric, being arranged one within the other. A similar portable gauge has been introduced by the Royal Air Establishment.[1] A mineral oil and coloured alcohol are the liquids employed. The same principle has been applied in the construction of a micro-manometer, composed of two vessels of large cross section containing liquids and connected by a narrow horizontal tube containing the same liquid, the movement of a globule of benzene or other suitable liquid, or a bubble of air, serving to measure the difference of level of the liquid in the two large vessels, such movement being amplified in the ratio of the cross section of the large vessels to the cross section of the narrow connecting tube. The zero positions of the surfaces of separation in such instruments are liable to change after pressure has been applied, and this defect is accentuated by globules of oil, etc., adhering to the tube.

For the measurement of differences of pressure of the order of 0·0001 in. of water, recourse may be had to the Chattock Tilting Micromanometer[2] (Fig. 84). In this gauge, a U-tube, of special design as shown, is mounted so that any displacement of water along the tube can be annulled by tilting the tube through a small angle whose value can readily be calculated. Errors due to capillarity and viscosity are thus avoided. As shown, the left limb of the U-tube is continued

[1] *Engineering*, 1917, 107, 395.

[2] *Phil. Mag.*, 1901 [vi.], 1, 83; *Engineering*, 12th Sept. 1913; *Proc. Inst. Civ. Eng.*, 22nd Dec. 1903.

upwards, and is concentric with the central vessel to which the right limb is connected. This central vessel is filled with oil and water by means of a tap communicating with an oil reservoir above. A surface of separation between oil and water is produced near the top of that part of the left limb contained in the central vessel. Such surface of separation is illuminated by light reflected from a small mirror, and can be observed by means of a microscope, or may be projected on a screen of ground glass. In the one case a cross wire in the eye-piece may serve as the constant datum point to which the surface of separation between oil and water is adjusted; in the other the surface of separation is throughout adjusted to a line ruled on the screen. Any motion of the surface of separation away from the fixed datum point is restored by a rotation of the large wheel, the circumference of which is divided into a number of equal parts, and which is carried by a screw, and from the amount of such necessary rotation the difference of pressure is readily obtained. The tap in the horizontal limb is employed to prevent rupture of the surface of separation by damping the motion of the liquid until approximate adjustment of the tilt has been achieved.

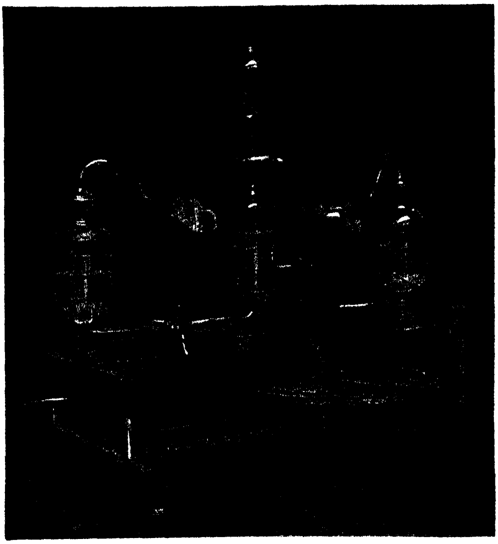


FIG. 84.

A somewhat similar micro-manometer, due to Töpler,[1] utilises a small column of xylene as the liquid, and the position of the column of liquid is always restored to its zero position in the tube by the tilting of the tube containing it, when a difference of pressure is established between the two ends of the column. The zero position is determined by exposure of the two ends of the column of liquid to the same pressure. In this form, the instrument is robust and portable, and the indications reliable.

Griggs has described a form of micro-manometer capable of measuring a pressure of $\frac{1}{5000}$ inch of water, and of very wide application in technical work.[2] The instrument consists of a narrow tube, which can be set at various inclinations to the horizontal and connected with a

[1] *Text-book of Practical Physics*, W. Watson, 1913, p. 143.
[2] *J. Gas Lighting*, 1912, **122**, 670.

reservoir of large cross section. The position of the meniscus in the narrow tube is read by a vernier. A micro-manometer, capable of measuring pressures up to two inches of water, has been designed by R. Threlfall.[1] The difference of the level of the liquid contained in two vessels of large cross section, connected by a tube of narrow bore, is ascertained from the reading of a micrometer screw adjusted to touch the surface of the liquid in one of the vessels. Readings can readily be made to 0·005 mm. of water. Fry[2] has described an exceedingly delicate type of micro-manometer in which two gas-tight chambers are separated by a gas-tight diaphragm. When a minute difference of pressure is established between the respective chambers, the consequent motion of the centre of the diaphragm at right angles to the plane of the diaphragm is determined by the rotation of a mirror attached to a bifilar suspension, one thread of which is attached to the centre of the diaphragm, and the other to a rigid support provided by the metal wall of the chamber. The instrument is calibrated empirically by the application of a series of known micro-differences of pressure, these being furnished by two columns of air subjected to different temperatures. The instrument had been adapted to furnish indications of rather larger micro-pressures[3] by the provision of a rubber-separating diaphragm, the motion of the centre of which is communicated to a pointer moving over a graduated arc. The Ogilvie instrument of this type gives a deflection of 300° of arc for a velocity

Type of Micro-manometer.	Principle employed.	Reference.	Minimum Pressure detectable by Micro-manometer
Rayleigh .	Tilting mercury U-tube .	*Phil. Trans.*, A., 1901, **196**, 205	0·68 dyne per sq. cm.
Morley and Brush	Tilting mercury U-tube .	*Amer. J. Sci.*, 1902, **13**, 455	0·68 dyne per sq. cm.
Threlfall .	Micrometer screw adjustments to surface of water U-tube	*Proc. Inst. Mech. Eng.*, 1904, p. 273	0·5 dyne per sq. cm.
Hering .	Tilting mercury U-tube with elec-contacts	*Ann. Physik*, 1906, **21**, 319	0·3 dyne per sq. cm.
Scheel and Heuse	Metal diaphragm with interference fringes	*Deutsch. Phys. Gesell.*, 1909, **11**, I., p. 1	0·1 dyne per sq. cm.
Chattock and Fry	Tilting water U-tube with benzene bubble indicator	Stanton, *Proc. Inst. Civ. Eng.*, vol. 156 Morrow, *Proc. Roy. Soc.*, 1905, A **76**, 205 Chattock and Tyndall, *Phil. Mag.*, 1910, **19**, 450 Fry and Tyndall, *Phil. Mag.*, 1911, **21**, 248	0·01 dyne per sq. cm.
Fry . .	Diaphragm	*Phil. Mag.*, 1913, **25**, 501	0·001 dyne per sq. cm.

[1] *Proc. Inst. Mech. Eng.*, **33**, 28.
[2] *Phil. Mag.*, 1913 [vi.], **25**, 494.
[3] Clift, *B. P.*, No. 1518, 1913; Ogilvie, *B. P.*, No. 13796, 1913.

of 100 feet per second. A recording micro-manometer, consisting of a large bell-shaped float to which a pen is attached, and floating in water, the surface of which is covered with a non-volatile liquid, has been introduced by the Cambridge and Paul Scientific Instrument Co. The differential pressure to which the inside and outside of the bell is subject is recorded on a chart rotated by clockwork.

The table on p. 172, given by Fry,[1] indicates the sensitiveness of various micro-manometers.

THE MEASUREMENT OF THE VELOCITY OF GASES IN PIPES

ANEMOMETERS

The velocity of a gas in a pipe or chimney is most frequently determined by means of the Pitot tube introduced by Pitot in 1732.[2] The use of the instrument is based upon hydrodynamical considerations which enable one to conclude that in the flow of a perfect fluid, if P = the pressure at any point, ρ the density of the fluid at that point, and v the velocity of the gas at that point, then under certain conditions

$$P + \tfrac{1}{2}\rho v^2 = \text{constant} \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

A more general relation than this is deduced from a consideration of the hydrodynamical equations, but for practical purposes, the relation as specified is sufficiently exact. It has been experimentally established that the relation $P + \frac{1}{2}\rho v^2 = C$, also holds for a viscous fluid. It follows from the above relation that if p = deficit of pressure due to the motion of the gas with velocity v, then

$$p - \tfrac{1}{2}\rho v^2 = o \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

The value of the constant in the above relation being the value of P when $v = o$. If, therefore, the deficit of pressure due to the motion is determined at any point in a gas stream, the application of (ii.) will allow of the calculation of v, provided the value of ρ is known.

The Pitot tube is employed to obtain the value of p in any given case, and consists of two tubes, one of which is bent at right angles so that its open end faces the current of gas or liquid, and the other has its open end arranged parallel to the direction of the flow of the gas or liquid. The former is known as the dynamic pressure-tube and the

[1] *Phil. Mag.*, 1913 [vi.], 25, 494.
[2] *Trans. Acad. Française des Sciences*, Nov. 1732.

other as the static pressure-tube. It is important to note that p in the relation (ii.) is the difference between the dynamic and static pressures *at the same point*, and the principal cause of error in the employment of the Pitot tube has been due to failure to realise this fact. It is obvious that the two tubes cannot be inserted so as to have their openings at the same point, and various approximations to this requirement have been made.

The form of Pitot tube shown in Fig. 85 has been designed as the result of experiments at the National Physical Laboratory, and using a tube of such form it has been shown that the relation $p - \frac{1}{2}\rho v^2 = o$ holds rigorously. The relation also holds rigorously when the static tube is placed so that its orifice is at the wall of the pipe.[1] The Pitot tube, in the form illustrated, consists of two tubes arranged concentrically, the inner tube being the dynamic pressure-tube and having a thin-lipped orifice arranged to face the current. The static outer tube has a conical closed end, and holes are drilled in it in a direction perpendicular to the axis of the cone. The difference between the static and dynamic pressure at the point, *i.e.*, the value of p, is determined by connecting the separate tubes to the branches of a micro-manometer of suitable delicacy. In general, the total pressure existing at the point of insertion of the Pitot tube may be considerable, and care must be taken that one limb of the gauge is not subjected to the pressure before the other. This can be achieved in a variety of ways, one of the simplest being by means of a doubly-bored tap with four limbs, arranged so that connection is simultaneously made to the two limbs of the micro-manometer on turning the tap in the appropriate manner.

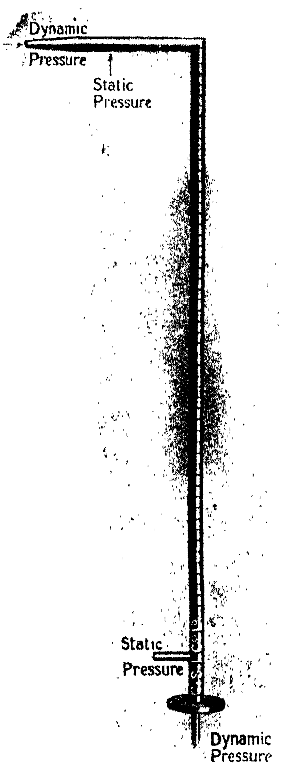


FIG. 85.

The formula $p - \frac{1}{2}\rho v^2 = o$ is applied as follows:—Consider the case of the flow of the air through a pipe, the weight of 1 cubic ft. of air under the conditions of temperature and pressure in the pipe being 0·0789 lb. The pressure, as indicated by the Pitot tube,

[1] Cf. *Proc. Inst. Mech. Eng.*, 1904, p. 280. *J. Gas Lighting*, 1912, **122**, 670, contains much useful information about the Pitot tube.

is found to be 0·0808 ins. of water. If v is the appropriate value of the velocity, then by converting the pressure to absolute units

$$\frac{0.0808}{12} \times 62.4 \times 32.16 = \frac{1}{2} \times 0.0789 \times v^2$$

$$\text{giving } v = 18.5 \text{ ft. per sec.}$$

In like manner the value of the velocity v corresponding to any determined value of p is calculated, care being taken that p is first of all converted to absolute units, the appropriate value of g and the density of the liquid employed in the manometer being chosen according to the system of units employed, whether c. g. s. or f. p. s. Similarly, the appropriate values of the density of the gas under the conditions existing in the pipe must be used.

It may be taken that, provided the flow of the gas in the pipe is

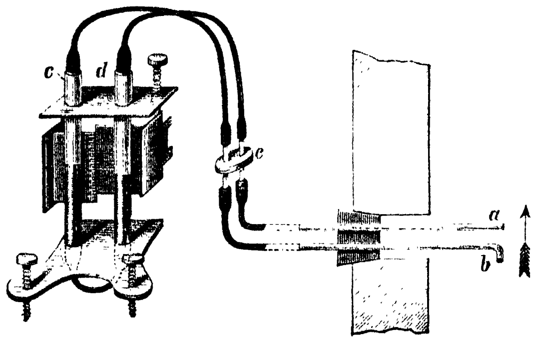


FIG. 86.

non-turbulent, the *mean* velocity of flow of the gas in the pipe can be ascertained by inserting the Pitot tube in the pipe so that the pressure is ascertained at a point distant two-thirds of the radius of the pipe from the axis. This result follows from theoretical considerations, and has been verified practically.[1]

The Fletcher anemometer is constantly employed in chemical technology, and is illustrated in Fig. 86. It will be seen that the static and dynamic pressures are not taken at points such that the relation $p - \frac{1}{2}\rho v^2 = o$ holds rigorously. The anemometer consists of two glass or brass tubes a and b, which are fixed air-tight, by means of a cork, into a suitable opening in the channel or chimney in which the velocity of the gas is to be measured, so that their ends are rather less than one-sixth of the diameter of the flue distant from its inner wall. The tube a, with the straight end, must be fixed as nearly normal as possible to the direction of the current, while the tube b must be so fixed that the

[1] *J. Gas Lighting*, 1912, **122**, 672.

gas stream blows direct into its open end. The tubes communicate, by means of rubber tubing, with the U-tube *cd*, which is half-filled with ether. The current of gas produces a rise in level of the ether in *d* and a fall in *c*. The resultant difference of level of the ether in the two limbs is measured by means of a millimetre scale and vernier; this is called the "anemometer reading." By turning the sliding disc *e* through 180°, *a* is connected with *c* and *b* with *d*; an equal difference of level to that previously recorded, but in the opposite direction, should now be obtained. In any case the mean of the two readings should be recorded as the final corrected "anemometer reading." The following tables facilitate the conversion of the anemometer readings to velocities in the case of air, ether being employed as indicating liquid in the manometer. Should any other liquid be employed in the manometer, and any other gas than air be flowing in the channel, the appropriate velocity can be readily calculated from those given by multiplying by the factor

$$\sqrt{\frac{\rho_l}{\rho_e} \times \frac{\sigma_a}{\sigma_g}}$$

where ρ_l = Density of liquid employed in manometer
ρ_e = Density of ether at same temperature as liquid
σ_a = Density of air
σ_g = Density of gas in question at 15° and 760 mm.

I.—Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in feet per second.

Column *a* gives the anemometer readings in inches; column *b* the velocity in feet per second at a temperature of 15° C. = 60° F., and barometric pressure 760 mm. = 29·92 inches.

a. Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.	*a.* Inches.	*b.* Feet per sec.
·01	2·855	·16	11·42	·32	16·15	·95	27·83
·02	4·038	·17	11·77	·34	16·65	1·00	28·55
·03	4·945	·18	12·11	·36	17·13	1·25	31·93
·04	5·710	·19	12·45	·38	17·60	1·50	34·97
·05	6·384	·20	12·77	·40	18·06	1·75	37·77
·06	6·993	·21	13·08	·45	19·15	2·00	40·37
·07	7·554	·22	13·39	·50	20·18	...	...
·08	8·075	·23	13·70	·55	21·17	...	...
·09	8·565	·24	13·99	·60	22·12	...	...
·10	9·028	·25	14·28	·65	23·02	...	...
·11	9·469	·26	14·56	·70	23·89	...	...
·12	9·891	·27	14·84	·75	24·73	...	...
·13	10·29	·28	15·11	·80	25·54	...	...
·14	10·68	·29	15·38	·85	26·32	...	...
·15	11·06	·30	15·64	·90	27·08	...	...

II.—Table for the Reduction of the Anemometer Readings to Velocity of Current, expressed in metres per second.

Column *a* gives the anemometer readings in millimetres ; column *b* the velocity in metres per second at a temperature of 15° C., and barometric pressure 760 mm.

a. mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.	*a.* mm.	*b.* m.
0·1	0·575	1·4	2·040	2·7	2·833	5·0	3·855	10·0	5·452	19·0	7·515
0·2	0·771	1·5	2·111	2·8	2·885	5·2	3·931	10·5	5·586	20·0	7·710
0·3	0·944	1·6	2·181	2·9	2·935	5·4	4·006	11·0	5·718	21	7·900
0·4	1·090	1·7	2·248	3·0	2·986	5·6	4·080	11·5	5·846	22	8·086
0·5	1·205	1·8	2·313	3·2	3·077	5·8	4·152	12·0	5·972	23	8·268
0·6	1·341	1·9	2·376	3·4	3·179	6·0	4·223	12·5	6·095	24	8·446
0·7	1·442	2·0	2·438	3·6	3·271	6·5	4·395	13·0	6·216	25	8·620
0·8	1·560	2·1	2·498	3·8	3·361	7·0	4·561	13·5	6·334	30	9·443
0·9	1·636	2·2	2·557	4·0	3·448	7·5	4·721	14·0	6·450	35	10·199
1·0	1·724	2·3	2·615	4·2	3·569	8·0	4·876	15·0	6·677	40	10·903
1·1	1·808	2·4	2·671	4·4	3·616	8·5	5·026	16·0	6·896	45	11·565
1·2	1·889	2·5	2·726	4·6	3·698	9·0	5·172	17·0	7·108	50	12·190
1·3	1·966	2·6	2·779	4·8	3·777	9·5	5·314	18·0	7·314	...	...

III.—Table for Correction for the Temperature at which the Anemometer Readings are made, to 15° C. = 60° F.

Column *a* gives the observed temperature ; column *b*, the factor by which the values in column *b* of Tables I. and II. must be multiplied, to give the correct velocity.

a. t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*	*a.* t° C.	*b.*
−10	1·046	18	0·995	42	0·956	66	0·922	140	0·835	260	0·735
− 5	1·036	20	0·991	44	0·953	68	0·919	150	0·825	270	0·728
0	1·027	22	0·988	46	0·950	70	0·916	160	0·815	280	0·721
2	1·022	24	0·985	48	0·947	75	0·912	170	0·806	290	0·715
4	1·020	26	0·981	50	0·944	80	0·903	180	0·797	300	0·709
6	1·016	28	0·978	52	0·941	85	0·899	190	0·788	320	0·697
8	1·012	30	0·975	54	0·938	90	0·890	200	0·780	340	0·685
10	1·009	32	0·972	56	0·935	95	0·884	210	0·772	360	0·676
12	1·005	34	0·968	58	0·933	100	0·878	220	0·764	400	0·654
14	1·003	36	0·965	60	0·930	110	0·867	230	0·756	450	0·631
15	1·000	38	0·962	62	0·927	120	0·856	240	0·749	500	0·603
16	0·998	40	0·959	64	0·924	130	0·845	250	0·742	...	...

Wherever possible, it is desirable to use, in place of the Fletcher anemometer, a Pitot tube of the form described on p. 174, in conjunction with a micro-manometer of suitable delicacy. The determination of the velocity of the gas stream is then effected in accordance with the method illustrated on pp. 174-175.

Hot-Wire Anemometry

The subject of hot-wire anemometry has been very considerably developed in recent years, and bids fair in time to displace anemometry by means of Pitot tubes, or the windmill type of anemometer. The subject has been developed theoretically and practically by King,[1] Morris,[2] Gerdien,[3] and Bordoni,[4] who have constructed instruments whereby practical hot-wire anemometry may be realised. The method, in essence, consists in submitting a heated, fine platinum wire to the cooling action of the current of gas, when the cooling effect of the current upon the wire serves as an indication of the magnitude of the gas current. Various methods whereby this result may be achieved are described in the memoirs to which reference is made. The application of the method has been extended to a wide range of gases by employing fine wires, surrounded by a coating of glass fused on to them.[5] The ordinary sensitiveness of the method employing such coated wires is ample for all technical purposes, and indeed little less than that afforded by the uncoated wire.

Various types of anemometers and indicators have been described by Pannell.[6] C. C. Thomas[7] has introduced a thermometric type of electric anemometer depending on the measurement of the supply of electric energy necessary to heat the stream of gas through a definite rise in temperature.

THE MEASUREMENT OF COLOUR: COLORIMETRY AND NEPHELOMETRY

The majority of the applications of colour measurement in technology is comprised of measurements whereby the amount of a component part of a mixture is quantitatively determined by the colour imparted by such component when in solution. As examples, one may give the colorimetric determination of nitrous acid, ammonia, and lead in water. In general, the determination is made by matching the colour of a solution of the component in question, in a suitable solvent, by comparison with the colour of a suitable standard solution. A psychical consideration is of importance in connection with colorimetry. The well-known psycho-physical Weber-Fechner law

[1] *Phil. Trans.*, A., 1914, **520**, 373; and *Phil. Mag.*, 1915, **29**, 556.

[2] *Brit. Assoc. Reports*, 1912.

[3] *Ber. deutsch. Physik. Ges.*, 1913, **20**, 961.

[4] *Nuovo Cimento*, 1912 [vi.], **3**, 241.

[5] *J. Soc. Chem. Ind.*, 1918, **37**, 165. See also *Proc. Phys. Soc.*, 1920, **32**, 196; *Phil. Mag.*, 1920 [vi.], **39**, 505.

[6] *Engineering*, 1919, **107**, 261, 295, 333, 363, 395.

[7] *J. Franklin Inst.*, 1911, **172**, p. 411.

states that: "In order that the intensity of a sensation may increase in arithmetical progression, the stimulus must increase in geometrical progression." The application of the law is made plain by illustration. A small difference of weight cannot be recognised when the weights compared are heavy, but the distinction can be readily made when the weights compared are light, and most easily, of course, when one of the weights itself constitutes the small difference. In just the same manner, technical colorimetry possesses the greater accuracy as the dilution of the solution is increased, and hence it is found that the practice of colorimetry is most highly developed in the detection of minute quantities, and of what may be classified as impurities. The application of the Weber-Fechner law is of importance in the construction of an empirical scale of shades of colour—say grey—by mixtures to which various shades of the colour in question, grey, are to be referred. In order that the scale when constructed—and it must necessarily be discontinuous—may be of equal "sensitiveness" throughout its range, then the admixture of the one colour, black in the present instance, to the other, white, must proceed by geometrical progression throughout the range.

Colorimetry

In the technical practice of colorimetry, the most commonly occurring determination is typified by the adjustment to equality of the "depth" or tint of colour of the solution to be examined, and that of a standard solution prepared according to an appropriate specification. In general, the adjustment to equality of tint is achieved in one of two ways: (1) the concentration of one liquid is varied until equality of tint results; and (2) the concentration of both liquids is maintained constant, the intensity of colour observed being varied by varying the depth of the column of liquid through which the light is transmitted.

Nessler's method for the determination of ammonia in water[1] is an example of the application of the first method. Here the standard solution is constituted of 100 c.c. of water free from ammonia, and the comparison solution is an equal volume of the water containing ammonia. The two solutions are contained in glass-stoppered bottles, preferably of cut glass, or glass cylinders about 20 cm. high and 4 cm. wide may be employed. To each, 2 or 3 c.c. of Rochelle salt solution are added, followed drop by drop by the same quantity of Nessler's solution (potassium mercury iodide) with shaking. A standard ammonium chloride solution, in which each c.c. is equal to 0·1 mg. NH_3, is then added to the contents of the vessel containing the

[1] Winkler, *Chem. Zeit.*, 1899, **23**, 454 and 541; 1901, **25**, 586.

ammonia-free water, until equality of tint of colour of the liquids in the two vessels is obtained. The ammonia content of the water to be examined is then readily ascertained from the result, being expressed in mg. per litre by the number of c.c. of ammonium chloride solution added. Standard tubes may be prepared, using varying quantities of standard ammonium chloride solution, or permanent standards may be prepared by mixing solutions of platinum and cobalt salts.[1]

Eggertz's method[2] of determining carbon in steel is an application of the same principle, the carbon content being determinable with an accuracy of 0·1 per cent. Britton[3] utilises fifteen standard solutions, representing carbon contents of from 0·02 to 0·03 per cent., and the test solution is compared with the nearest of these standards. The consideration already deduced on the basis of the Weber-Fechner law should apply to the preparation of these standard solutions.

The second method of procedure is instanced by Stead's colorimetric method for the determination of carbon in steel.[4] Here 1 g. of a standard steel of known carbon content and 1 g. of the test metal are separately dissolved in nitric acid of sp. gr. 1·2 at 90° to 100°; to each solution 30 c.c. of hot water and 13 c.c. of sodium hydroxide solution of sp. gr. 1·27 are added, the liquids thoroughly shaken and made up to 60 c.c., allowed to settle for ten minutes, and filtered. A 50 mm. column of the standard solution is then passed into one graduated tube, and the height of the test solution in a similar tube adjusted, so that the tints appear of equal intensity when the tubes are illuminated from below.

It is established in the theory of the absorption of light, that if I is the intensity of the light at any point in a homogeneous absorbing medium, and dI the diminution of the intensity due to passage through a thickness dx of the medium, then :—

$$\frac{dI}{I} = -Kdx$$

where K is a constant for any given medium, but varies from one medium to another.

Integration of the above relation gives :—

$$\int_1^2 \frac{dI}{I} = -\int_1^2 Kdx$$

and hence

$$\log_e \frac{I_2}{I_1} = -Kt$$

[1] Report of American Committee on Water Analysis, *Journal of Infectious Diseases*. Supplement No. 1, May 1905, pp. 16-19.

[2] *Chem. News*, 1881, **44**, 173.

[3] *Chem. News*, 1872, **26**, 139.

[4] *J. Iron and Steel Inst.*, 1883, p. 213; *Chem. News*, 1883, **47**, 285.

where t is the thickness of medium through which the light passes, while its intensity is reduced from I_1 to I_2. Now in the case of the two tubes employed above, adjustment is made so that the incident light is the same in each case, and moreover, the emergent light is adjusted to equality in each case. Under these conditions $\log_e \frac{I_2}{I_1}$ possesses the same value in each case, so that if the suffix a refer to the one tube and β to the other, then:—

$$K_a t_a = K_\beta t_\beta$$

hence

$$\frac{K_a}{K_\beta} = \frac{t_\beta}{t_a}.$$

Now the value of K is obviously proportional to the density of the absorbent matter in the liquid, and hence it is concluded that the percentages of carbon are inversely proportional to the lengths of the columns of liquid when the emergent beams are adjusted to equality.

This principle is applied in a variety of colorimetric instruments. A simple form of colorimeter is shown in Figs. 87 and 88. In this, all light is cut off except the small amount diffused through the ground glass at the bottom of the front side, which is transmitted through the tubes after being reflected by the slip of ground white glass C. The light metal shade is made to fit one or both eyes closely at the discretion of the operator, and can be removed to manipulate the tubes. A thin metal partition separates the tubes, all is painted dead black, and the light which enters is diffused to prevent reflection on the polished sides of the tubes as much as possible. Matching of the colour of any given liquid against a standard solution is readily achieved by varying the respective depths of the liquids in the tubes. The apparatus is especially applicable to the colorimetric determination of copper, iron, ammonia, titanium, and bismuth.

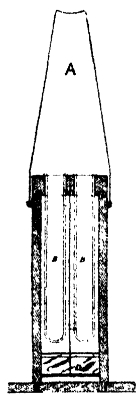


FIG. 87.

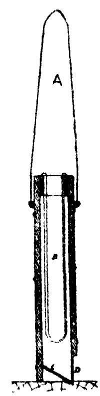


FIG. 88.

A.—Metal shade.
B.—Glass tubes to contain liquids for comparison.
C.—White ground glass reflector.
D.—Transparent ground glass.

T. W. Burgess[1] has described a simple form of tintometer which is useful when a large number of samples of water of similar origin have to be compared. It consists essentially of two tubes, each two feet long, one of which is filled with distilled water, and the other with the water under observation. The light passing through these is reflected upwards through two short cylinders, and the colour of

[1] *Analyst*, 1902, 27, 295.

the water matched with a standard coloured solution in the cylinder above the distilled water tube. The standard solution is made by dissolving 1 g. of crystallised cobalt sulphate and 0·05 g. of potassium bichromate in 1000 c.c. of water.

The colorimeter designed by C. H. Ridsdale is similar in principle.[1] In this instrument three glass tubes are arranged vertically in a vertical plane near one another, and at their lower ends are provided with a small opaque white cylinder. The central tube can be removed and is closed below. The bottom parts of the outer tube are drawn out and pass through india-rubber bungs into ruby glass bottles containing standard solutions of different strengths. The liquid to be examined is placed in the central tube. The ruby glass bottles are provided with syringes, whereby the standard solutions in the outer tubes can be adjusted to any desirable heights. A mirror is adjusted above the three tubes. By means of this mirror the tint of the opaque cylinder mentioned is observed by light which has traversed each of the solutions, and the height of liquid in the separate tubes is adjusted so that equality of tint is secured. The strength of the solutions are then inversely proportional to their respective lengths. Ridsdale[2] has produced a modification of his apparatus applicable to solutions of deeper tint than can be used in the foregoing apparatus. Colorimeters employing the same principle have been introduced by Stokes,[3] Kennicott Sargent,[4] Gunsberg.[5] A variation in application is due to Autenreith and Kœnigsberger,[6] in which equality of tint is obtained by moving across the beam of light a wedge-shaped vessel containing the test solution, and adjusting the position of the wedge so that equality of intensity is secured between the light transmitted through the wedges and that transmitted through a trough of standard solution alongside. The instrument is specially designed for the determinations of hæmatine in blood, but can be equally well employed for the determination of nitric acid, iodine, chromium, titanium, etc. In Schreiner's colorimeter,[7] for convenience of comparison, the coloured discs produced by the transmission of white light through the separate tubes are brought into juxtaposition. Patterson[8] has designed a colorimeter in which the separate discs are brought into juxtaposition by the use of total reflection prisms, and as in Schreiner's instrument, the lengths of liquid through which the beams are transmitted are varied by raising or lowering a flat-bottomed tube containing the liquid in a wide tube containing the same liquid. By the use of a spectroscopic eye-piece, the absorption

[1] *J. Soc. Chem. Ind.*, 1886, **5**, 586.
[2] *J. Soc. Chem. Ind.*, 1888, **7**, 70.
[3] *J. Soc. Chem. Ind.*, 1887, **6**, 135.
[4] *Chem. Engineer*, 1907, p. 213.
[5] *J. Dingl. polyt.*, **228**, 457.
[6] *Chem. Zentr.*, 1916, **1**, 2032.
[7] *J. Amer. Chem. Soc.*, 1905, **27**, 1192.
[8] *J. Soc. Chem. Ind.*, 1890, **9**, 36.

spectra can be compared, and in the paper referred to examples are given of the varied possibilities of application of such an instrument in practice. Colorimetric quantitative analyses of mixtures are readily carried out by the use of the instrument so arranged.

The colorimeter is largely used in the oil industry, and two forms of colorimeter employed therein have been introduced by A. Wilson and C. Stammer respectively.

Wilson's colorimeter consists of a box, the lid of which may be clamped at any angle and acts as a stand for two brass tubes *b* (Figs. 89 and 90), 16 in. long, holding the oil and the standard glasses respectively. Both tubes are closed by thin glass plates fixed in screw-caps. A mirror at the bottom of the lid reflects the light through the tubes and through a pair of prisms into the eye-piece. The field, as seen through the eye-piece, is divided by a sharp line which allows of

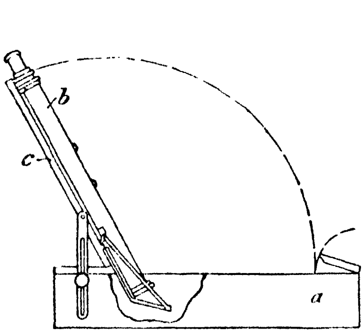


FIG. 89.

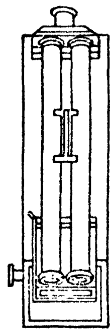


FIG. 90.

the comparison of the two halves of the field, which are tinted respectively with the colour of the oil and that of the standard. A series of four standard glasses is supplied with each colorimeter, corresponding, in ascending order of depth, to the four commercial grades—water-white, superfine white, prime white, and standard white.

In making a determination one of the tubes is filled with oil, the other remaining empty. The tubes are first fixed in position; one half of the field seen through the eye-piece will now, of course, be darker than the other. Standard glasses are then inserted in the empty tube, until both halves of the field have approximately the same tint. The grade of the oil is thus fixed.

Stammer's colorimeter has the advantage over that of Wilson that it allows of the variation of the length of the column of oil measured, whereby the shade of colour can be more accurately defined.

The construction of this apparatus is shown diagrammatically in Fig. 91. A fixed tube *z*, on which is placed a standard glass plate *u*,

is arranged side by side with a cylinder *c* in which the oil is placed; this cylinder can be moved up and down by means of the hand-wheel *k*, whereby the length of the column of oil under comparison is varied at will. Both *z* and *c* are closed at the bottom by thin glass plates through which the light reflected from the mirror *p* reaches the eye-piece *o*. The length of the column of oil is adjusted until both fields, as seen through the eye-piece, have the same depth of tint, and this length is measured on the scale *m*.

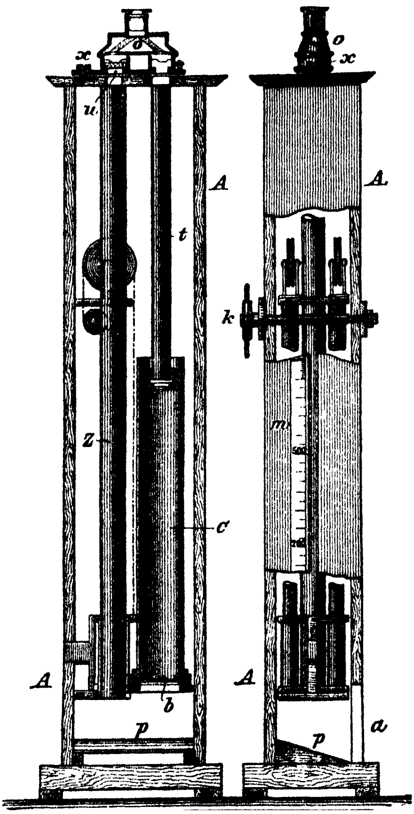


FIG. 91.

The use of the single glass standard was found by Boverton Redwood[1] to be open to objection, as the sensitiveness of the test was much impaired when the column of oil had to be greatly shortened for the comparison. Modifications introduced by R. Redwood have overcome this defect.

J. W. Lovibond[2] has designed an instrument which he terms a "tintometer," whereby any colour may be readily determined and registered. The instrument is illustrated in Fig 92. It consists of a parallel-sided box, divided by a central taper partition B, terminating in a knife-edge at the eye-piece C. This knife-edge, being inside the range of vision, is not seen when the instrument is in use. At the other end of the instrument are two apertures D, D, of equal size, alterable in size and shape by means of diaphragms. They are separated by the thick end of the central partition B, which, together with the sides, is recessed by grooves. The instrument is arranged so that the only light which can reach the eye passes in equal quantity on each side of the partition, illuminating the object under examination on one side and standard glasses inserted for the purpose on the other. The substance to be examined, if a liquid, is contained in a square cell arranged within one of the divisions, and suitable standard glasses are inserted in the other division, so that on looking through

[1] Cf. *Petroleum and its Products*, 3rd ed., 1913, vol. ii. p. 215.

[2] *J. Soc. Chem. Ind.*, 1888, 7, 234; 1890, 9, 10; 1891, 10, 489; 1909, 28, 500.

the eye-piece, shaded to prevent access of side light to the eye, the tint visible through each division is the same. The standard glasses consist of coloured slips cut to fit the grooves of the instrument. The slips are arranged in series, all those in each series being of the same colour, but being of different depth of colour. The variation of the depth of colour is in regular degrees, each degree

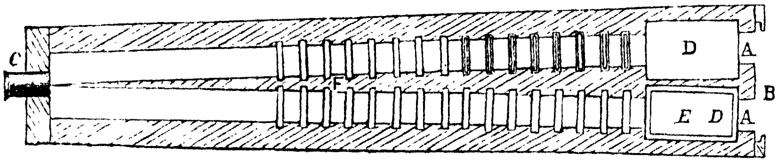


FIG. 92.

being of the same tint value as that chosen for the unit of the series. Thus a single slip of 10 degrees tint value has the same value as 10 glasses of 1 degree. Every slip is, moreover, marked with the corresponding number of degrees or tint number, and also with a denominational or colour number showing to which series the slip belongs. The units in various depths of colour are chosen so as to be consistent with the possibility of the addition of a single unit being distinguishable in the deeper shades; in the lighter shades, in accordance with principles already referred to, subdivision of the unit is accordingly possible.

When the colour of a fabric is to be estimated, this is stretched on a block and placed in one division, and a white fabric of similar texture prepared with a plate of pure plaster of Paris is placed in the other. The standard plates are then inserted as described until the two divisions as viewed through the eye-piece appear of the same tint, when light reflected from the fabric and from the sheet of plaster of Paris respectively pass down the compartments. Powders, sugar, etc., pressed in a small tray are similarly examined. For very accurate observations, the intensity of the light employed may be determined before commencing by closing one division, and placing in the other as many slips of neutral tint as serve to obstruct all light. By the substitution of a movable wedge of coloured glass for the standard plates, the apparatus becomes immediately available for ordinary colorimetric determinations. An improved form is binocular, and is suitable for tests of colour vision. The instrument is supplied together with tintometer sets suitable for use by dyers and printers, for fabrics and solids, for determination of sugar and caramel, for water analysis, for determination of carbon in steel, and for determination of the colour in tanning solutions, petroleums, oils, waxes, lards, flour, etc. Spielmann and Wood have used the tintometer for the determination of cyanogen

compounds in concentrated ammonia liquor.[1] The application of the instrument is seen to be extremely wide. Konig [2] has devised a method of colorimetry for the estimation of metals, dependent upon the depth of colour imparted to a borax bead of known weight by a measured quantity of the oxide of the metal.

NEPHELOMETRY

Nephelometry is distinguished from colorimetry by the fact that the former is concerned with the comparison of *scattered* radiations, whereas the latter is concerned with the comparison of *transmitted* radiations. It is well known that when a beam of light is incident in a dust-laden atmosphere, the individual particles of dust in the beam are clearly seen when viewed in a direction at right angles to the direction of propagation of the beam. The particles scatter a portion of the light incident upon them, and Lord Rayleigh [3] has shown how the intensity of the beam of light scattered in any direction is to be calculated from the physical characteristics of the particles and of the medium in which the particles are suspended. The necessary precautions indicated by theoretical considerations for the comparison of the intensities of scattered radiations have not, in general, been taken into account in nephelometric work. Invariably the suspensions are illuminated by non-homogeneous light, and usually no precaution is taken to obtain equality of size of the scattering particles. The main difference between the practice of colorimetry just described and that of nephelometry consists in the fact that in nephelometry the radiation is incident on the suspension in a direction of right angles to the direction in which the suspension is viewed, whereas in colorimetry the direction of vision corresponds with that of the incident radiation. Nephelometry is accordingly applied to the measurements of suspensions in opalescent liquids, special reagents such as starch solution, stearic acid or gelatin being added to maintain the precipitates in the form of suspended colloids.

Details of nephelometric determinations have been given by Mulder,[4] Stas,[5] Richards and Wells, and others.[6] Richards and Wells have detailed all the precautions necessary for accurate nephelometry, and have described an arrangement whereby exact nephelometry is possible.[7] Their nephelometer is shown in Fig. 93. It consists of two test tubes arranged almost vertically, but slightly

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 43 T; see also *Alkali Inspector's Report*, 1906, p. 42.
[2] *Proc. Amer. Phil. Soc.*, **18**, 7, 29, 184, 208, 211. [3] *Phil. Mag.*, 1871 [iv.], **41**, 107, 274.
[4] *Die Silber Probiermethode*, 1859, p. 53, Grimm, Leipzig. [5] *Oeuvres*, 1894, **1**, 155.
[6] *Proc. Am. Acad.*, 1894, **30**, 385; *J. Amer. Chem. Soc.*, 1905, **27**, 459.
[7] *Amer. Chem. J.*, 1904, **31**, 235.

inclined toward one another, so that the eye can look into both. Around the test tubes are two opaque sliding jackets. When the slides are adjusted so as to give equal opalescence in the two tubes, the precipitate is taken as being inversely proportional to the lengths of tube exposed to the light. This relation does not hold accurately for dense precipitates, since the nearer portion partly hides the portion more distant from the source of light, but with slight opalescences, the error is not great, especially when the lengths are not very different. There are three separate parts to the nephelometer, the main frame A, which holds the tubes in position, a movable top B containing adjustable prisms, and a large box C in which is the source of light. The tubes to hold the solutions are of clear glass, free from striations, and contain 0·032 litre of the respective liquids. They are painted outside, round the top and bottom, with black asphalt paint. These opaque bands form the most convenient method of obliterating reflections from the meniscus and the curved bottom of the test tube. The space between the lower edge of the upper band and the bottom of the tube is the same in each case. The lower edge of the upper band projects below the wooden support P in order to provide a sharp line of demarcation between light and darkness, as well as to allow the tubes to be shut into complete darkness by the sliding tubes S, S. The tubes rest upon equal wooden pillars (which guide the sliding jackets), and project well above the support P in order to preserve their cleanliness. The jackets are of glass, thickly painted, and are moved up or down as desired, being finally held in any desired place by a brass spring. When the jackets are raised, they disclose below two scales which indicate exactly the lengths of the tubes above exposed to the light. Upon the frame rests the small box B, which shuts out all light, and is yet easily removable. In the box is contained a small frame which can be adjusted in any desired position by means of the set screw R. The frame carries two 15° prisms, with their thin edges ground so that they fit closely. On looking downwards through the prisms, semi-circular images of about half of each test tube are brought into view side by side, and together appear scarcely larger than a single tube, the dividing line between being scarcely visible. The success of the instrument depends upon this arrangement of

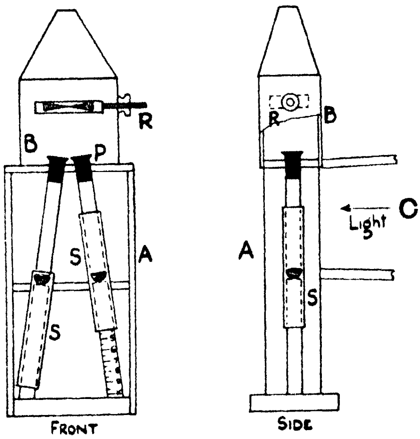


Fig. 93.

prisms. It is found that, with practice, successive readings of the scales by one observer will not differ by as much as a millimetre.

The principal possibility of error lies in the state of the precipitated material held in suspension. Wherever possible, the state of the suspension in the two tubes should be exactly the same, and to this end the compared suspensions should, wherever possible, be obtained in the same way, and the solutions stirred from time to time. The average of many results is within one or two per cent. of the truth, and the instrument is capable of detecting one part of silver chloride in 30,000,000 parts of water.

According to P. A. Kober,[1] the principal source of error in nephelometry is an instrumental one, due to the diaphragms or openings at the top of the eye-piece being too large. As pointed out in connection with colorimetry, the application of the Weber-Fochner law leads to the deduction that nephelometric determinations are possible with the greatest accuracy in dilute suspensions, and in general the strength of the suspension should not exceed 100 mg. per litre. Nephelometric determinations are to be preferred to colorimetric when the suspension is only slightly coloured; when the suspension is highly coloured, a colorimetric determination is to be preferred. The varied applications of nephelometry are detailed by Kober, including the determination of ammonia, acetone, fats and oils, proteins, calcium, and phosphorus as representative of the extremely large number of possible applications.

REFRACTOMETRY: THE MEASUREMENT OF REFRACTIVE INDEX

The refractive index of a substance is a physical property which may be employed for the characterisation and analysis more especially of liquids and solutions. That its use for this purpose has become very general only recently, is mainly due to the fact that the earlier standard methods for measuring the refractive index of a liquid were too complex for the requirements of the analyst.[2] It was not until the spectrometer and hollow prism were replaced by the critical angle refractometer that the accurate measurement of refractive power could be made with reasonable rapidity, and become of practical utility in the chemical laboratory.

When a ray of light is incident at the interface separating two media,

[1] *J. Soc. Chem. Ind.*, 1918, 37, 75.

[2] *Cf.* J. C. Philip, *J. Soc. Chem. Ind.*, 1919, 38, 139 T. The same volume of the *J. Soc. Chem. Ind.* contains a valuable series of contributions on "Refractometry and its Applications in Technical Analysis," pp. 139 T-150 T.

it is, in general, transmitted in the second medium in a direction different from that of its path in the first medium. The laws relating to this so-called refraction of light were first stated by Snell in 1621. He showed that the angle of incidence i is related to the angle of refraction r, by the relation $\frac{\sin i}{\sin r}$ = a constant determined by the natures of the media of incidence and refraction. If the second medium is the optically denser medium, the refracted ray approaches more nearly to the normal than is the case with the incident ray. The value of the ratio $\frac{\sin i}{\sin r}$ is found to depend upon the character of the light in the incident ray. If the incident ray is composite, *i.e.*, if

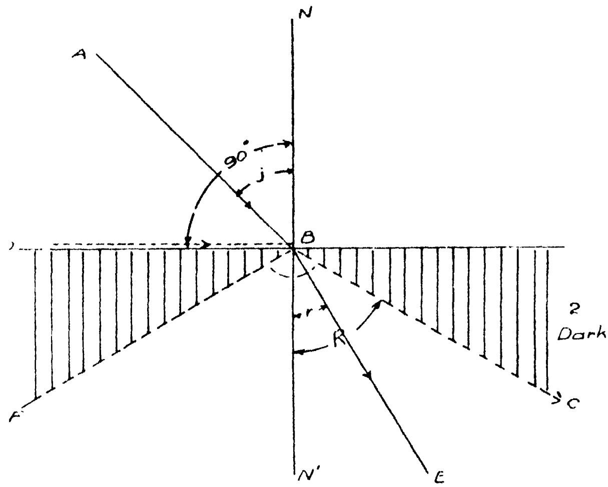


FIG. 94.

the incident radiation can be resolved into constituents of different wave-lengths, then different values of r for a constant value of i will be obtained for each of these different constituent wave-lengths. The refracted ray in this case will be spread out into a so-called spectrum, and the phenomenon is termed dispersion.

In the case of a homogenous incident ray, the constant ratio $\frac{\sin i}{\sin r}$ is termed the refractive index of medium 2, with respect to medium 1. If medium 1 is a vacuum or air, it is customary to refer to the corresponding value of $\frac{\sin i}{\sin r}$ as the refractive index of medium 2. It is clear that if a ray is incident along DB (see Fig. 94), corresponding to grazing incidence ($i = 90°$), the refracted ray in the denser medium 2 is such that, medium 1 being air, $\frac{\sin 90}{\sin R} = n$, the refractive index of

medium 2. Furthermore, the refracted ray BC, under these conditions, marks the boundary separating the dark region to the right of BC from the bright region to the left, when the point B is illuminated by rays incident at all angles of incidence included between 0 and 90°. When the light is incident in the second or denser medium along CB, no light emerges into the upper medium 1. A like phenomenon arises if the angle of incidence in the denser medium 2 is greater than the angle R (= N′BC). This phenomenon is known as total reflection, and the angle R is known as the critical angle. Where the critical angle R is determined between two media, one whose refractive index n is required to be measured and the other of refractive index N, it is easy to show that

$$\frac{n}{N} = \sin R \quad \text{or} \quad n = N \sin R.$$

This is the fundamental relation of refractometry employing the limiting ray or critical angle.

The refractometer in which the fundamental relation $n = N \sin R$ is most directly employed is that of Hans Heele.[1] In this the limiting ray is incident at the plane interface separating the liquid, whose refractive index is required, from a sphere of heavy glass. The point of illumination is the centre of the sphere, so that no refraction occurs on the ray emerging into air, and the relation $n = N \sin R$ is directly employed. It is obvious that the instrument can only be employed for substances for which n is not greater than N, the maximum value of sin R being 1. This rule is of general application to the various types of refractometers utilising the existence of the limiting ray.

The refractometers most commonly employed in technology comprise (1) Pulfrich's refractometer; (2) Abbe's refractometer; (3) the Butyro-refractometer, and (4) the Dipping refractometer.

The Pulfrich Refractometer.[2]

Essentially this instrument (Fig. 95) consists of a rectangular glass prism, mounted so that of the two faces at right angles to one another, one, PQ, is horizontal, the other, QS, vertical. The liquid, whose refractive index is required, is contained in a small glass vessel cemented to the horizontal prism face. PQ is illuminated by monochromatic light furnished by a vacuum tube or a flame containing a bead of sodium chloride, etc. The path of the limiting ray is indicated by ABCD. In this case $n = N \sin R$ where N = refractive index of

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 773.

[2] See Guild, *Proc. Phys. Soc.*, 1918, **30**, p. 30. Note on the Pulfrich Refractometer.

the material of the prism. The angle of emergence of the ray from the prism being i, then

$$\frac{\sin i}{\sin(90 - R)} = N.$$

Hence

$$\cos R = \frac{\sin i}{N}$$

and $$n = \sqrt{N^2 - \sin^2 i}.$$

The value of N, at the appropriate temperature being determined once for all (it may be remarked that a secular variation of N of very small amount is possible), a determination of the value of i, the

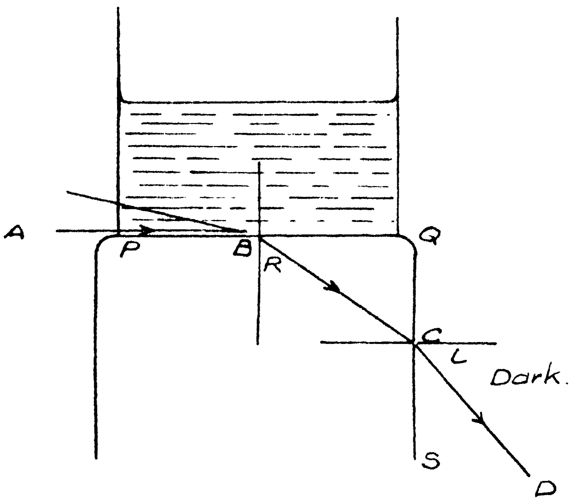


FIG. 95.

angle of emergence of the limiting ray, suffices for the determination of the refractive index of the liquid employed. The instrument enables determinations of refractive indices to be made with an accuracy of one unit in the fourth decimal place.

As the refractive index of all liquids varies with temperature, the general value of $\frac{dn}{d\theta}$, *i.e.*, the variation of n per degree, being about 0·0005, it is clear that to enable the possibilities of the instrument to be satisfactorily utilised, temperature regulation correct to 0·2° is essential.[1] It is questionable whether this degree of temperature control is usually attained. The general practice consists in passing a current of water of regulated temperature through the mounting of the

[1] See Simeon, *Proc. Phys. Soc.*, 1918, p. 30—"The Accuracy attainable with Critical Angle Refractometers."

prism, and through a silver vessel lowered into the cell containing the liquid.

The appearance of the instrument is shown in Fig. 96. The prism mount is shown at L, the liquid under examination being contained in the hollow glass cylinder above. The stream of water, at regulated temperature, circulates as indicated by the arrows, passing into the silver vessel S and the prism mounting. Monochromatic illumination may be furnished by such means as a coloured flame, a mercury arc, Geisler tube, etc., any desired wave-length being satisfactorily isolated

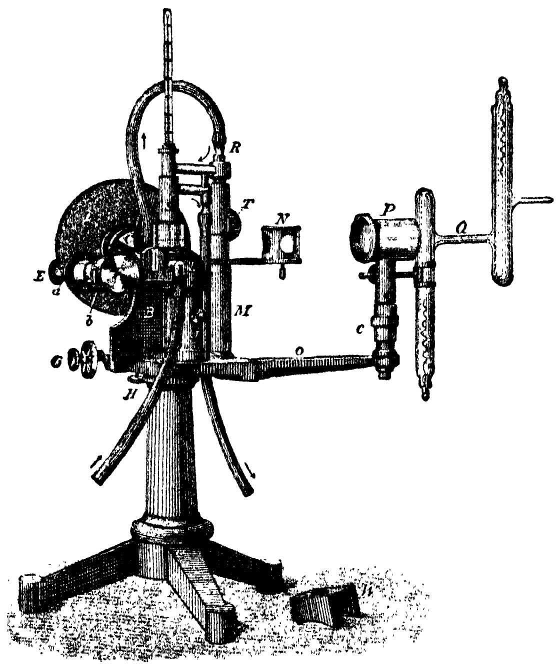


Fig. 96.

by means of the appropriate screen, of which a large number are produced by Messrs Wratten & Wainwright. The auxiliary prism N is employed for directing the light from a flame used as source, on to the prism of the refractometer. It must be remembered that the value of the refractive index determined is appropriate only to the wave length of the light employed. The telescope EF is fixed to the divided circle D and rotates with it. The latter may be clamped in any desired position, and a fine adjustment of the cross wire to the line of demarcation between light and dark effected by means of the tangent screw G. The tangent screw carries a drumhead enabling the dispersion of any liquid to be accurately determined.

The refractive index of solid bodies may be readily determined by

means of the Pulfrich's refractometer. For this purpose the hollow glass cylinder is removed, and the solid brought into optical contact with the prism face by interposing a film of suitable liquid of high refractive index, such as α-monobromnaphthalene. The procedure is then exactly as already described. The refractive indices of doubly refracting crystals in any desired direction relative to the optic axes can likewise be readily determined in this manner

The Abbe Refractometer.

It is readily seen that the range of refractive indices measurable by means of a refractometer of the Pulfrich type is restricted by the fact that the position of the prism is fixed. An extension of the range of refractive indices capable of measurement is secured by the use of the Abbe Refractometer (Fig. 97). In this, a double prism capable of being rotated about a horizontal axis is employed. The double prism is composed of two prisms of dense flint glass. The prisms are mounted in hollow metal cases, through which a current of tempered water is maintained. The interior faces of these water jackets are gilded to prevent corrosion.

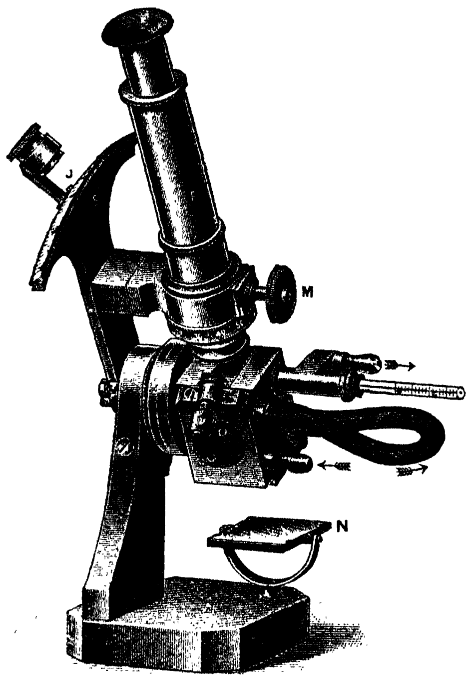


FIG. 97.

To determine the refractive index of a liquid the double prism is opened and a drop or two of the liquid placed on the ground surface of the lower prism. The prisms are then brought together and clamped. By means of the mirror N a beam of light is caused to illuminate the ground surface of the lower of the two prisms. Light is scattered in all directions by the various points of the ground surface, and provided the refractive index of the upper prism is greater than that of the liquid being investigated, the rays entering the film at grazing incidence will be refracted through the prism, emerging as parallel rays. These rays, brought to a focus by means of a

telescope, mark the boundary between light and dark. It can be shown that if:—

N = Refractive index of the upper glass prism.
A = Refracting angle of upper prism.
α = Angle made by limiting rays with normal on emergence from prism,

then n, the refractive index of the liquid $= N \sin\left\{A - \sin^{-1}\left(\frac{\sin\alpha}{N}\right)\right\}$.

Either monochromatic or non-monochromatic light may be used. The employment of white light is made possible by the use of a compensator whereby the effects of the dispersion due to the liquid and prism are neutralised. The compensator consists of two direct-vision Amici prisms rotated by means of the milled nut M, in opposite directions. A colourless border-line separating the dark and bright fields is thus obtained, and the double prism is turned by the arm J so that this line of separation, sharply focussed, is made to coincide with the cross wire of the telescope. The refractive index of the liquid can then, if necessary, be calculated by means of the above formula, but in the instrument the refractive index is directly read off on a divided scale rigidly attached to the arm carrying the double prism. This scale moves with the arm past a vernier scale, and the appropriate refractive index is found against the zero of the scale.

A measurement of the dispersion of the liquid can be obtained by reading the drum of the compensator when colour compensation at the border-line is secured, reference being then made to tables supplied with the instrument.

The Abbe instrument has a scale of refractive indices extending from 1·3000 to 1·7000 and the accuracy of reading is 0·0001. A test piece of glass of known refractive index serves to check the scale of the instrument from time to time. The instrument is largely employed in the examination of liquids such as aniline, milk, sera, etc., and can be readily employed for the examination of oils and fats. The butyro-refractometer, however, has largely displaced the Abbe instrument for the examination of these latter materials.

The Butyro-Refractometer.

This instrument (Fig. 98) resembles the Abbe in some respects. The two prisms, as in the latter instrument, are mounted in double-walled water jackets, and the upper prism A is rigidly attached to the telescope K. The prism A also is constructed so that an achromatic line of separation is obtained in the eye-piece of the telescope when pure butter is used between the two prisms, white light being employed for illumination. The scale of the instrument

is fixed in the focal plane of the objective, and reads from −5 to +105 corresponding with refractive indices for sodium light from 1·42 to 1·49. The position of the border line with respect to the scale is read in some instruments on a micrometer screw, and the corresponding refractive index obtained by reference to the table. Elimination of colour at the border-line being only

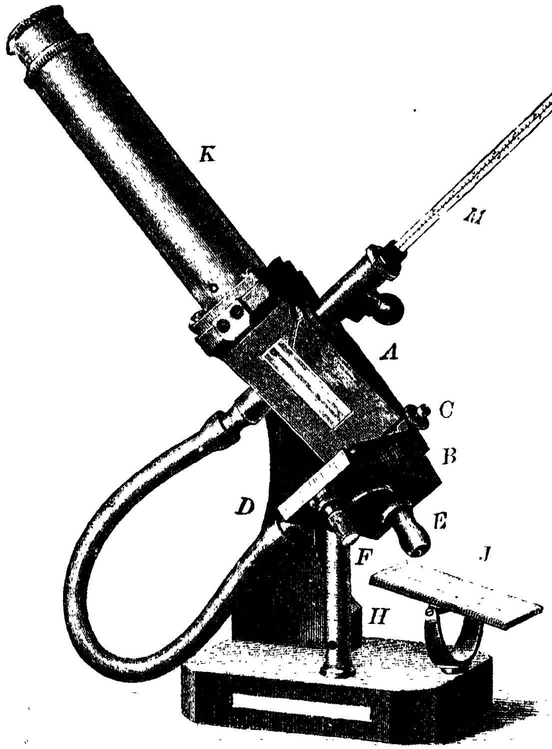


FIG. 98.

possible in the case of pure butter fat, the border-line, as usually obtained, is coloured. A blue fringe indicates a fat of higher, and a red fringe a fat of lower, dispersive power than pure butter. The temperature usually employed is 40°. If not taken at 40°, the readings are usually corrected for temperature by adding 0·55 division to the reading for every degree above 40°.[1] The scale of the instrument can be adjusted by means of a key, and is checked by ascertaining the refractive index of the standard liquid supplied with the instrument, at a series of temperatures. The divisions of

[1] Cf. *J. Amer. Chem. Soc.*, 1904, **26**, 1193; *Analyst*, 1907, **32**, 44.

the scale of the instrument correspond to the following refractive indices:—

Divisions on Scale.	Refractive Index.	Difference.
0	1.4220	
		0.0080
10	1.4300	
		0.0077
20	1.4377	
		0.0075
30	1.4452	
		0.0072
40	1.4524	
		0.0069
50	1.4593	
		0.0066
60	1.4659	
		0.0064
70	1.4723	
		0.0060
80	1.4783	
		0.0057
90	1.4840	
		0.0055
100	1.4895	

The instrument enables refractive indices to be determined correct to 0·0001.

The Dipping or Immersion Refractometer.

In this type of refractometer, a prism is mounted at the lower end of a viewing telescope, the prism itself being immersed in the liquid whose refractive index is required (Fig. 99). White light reflected from a mirror suitably placed falls at grazing incidence on the brightly polished face of the prism when immersed in the liquid, and in accordance with the principles enunciated above, the field of vision is divided by a boundary of separation between light and dark portions, such boundary being determined by the paths of the limiting rays in the prism, which are ultimately focussed in the focal plane of the eye-piece of the telescope. A pair of direct vision prisms is provided between the prism and the telescope objective. The prisms can be rotated by means of a milled nut, whereby coloration of the boundary line is compensated. The scale of the refractometer is situated at the focal plane of the eye-piece and is graduated from − 5 to + 105. The boundary line is sharper than in the Abbe instrument, and this renders possible the use of a telescope of higher magnifying power than that ordinarily employed with the Abbe type of instrument. The position of the boundary line is read to 1/10th of a division by means of a micrometer screw. In the original form of dipping refractometer, the prism was cemented

into the telescope body, and this introduced many difficulties of operation. The range of refractive indices to which the instrument was applicable was also an extremely restricted one (1·32539 to 1·36640 for sodium light). The Abbe instrument possesses a range 1·3000 to 1·7000 for sodium light. The accuracy possible with the dipping refractometer is, however, 0·00003 compared with 0·0001 with the Abbe instrument. The range of the dipping instrument has been

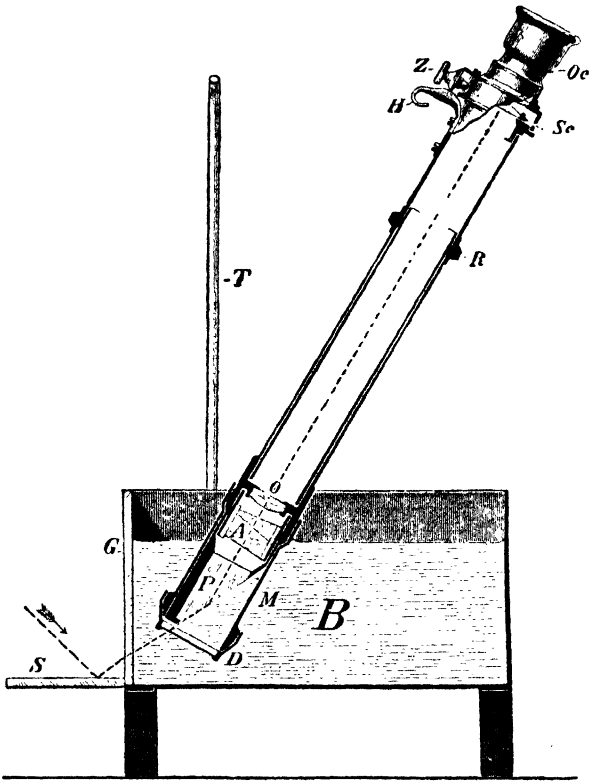


FIG. 99.

extended to a refractive index 1·55 for sodium light by Messrs Bellingham and Stanley, by the provision of a series of prisms of suitable refractive indices, such prisms being easily affixed to the telescope body as required, and tightness being assured by the provision of a washer of rubber or lead, etc. It is interesting to note that the refractive index of ordinary water varies slightly with its content of dissolved substances. Thus the value of n for town water is greater by 0·00004, and for pure distilled water saturated with carbon dioxide at atmospheric pressure, less by 0·00003 than the value of n for distilled water; such variations are just within the possibilities of measurement of the instrument.

The temperature of liquids examined is generally regulated to 17·5° by immersion of the beaker containing the liquid in some form of bath controlled by a thermostat, time being given for the prism to attain the same temperature after immersion in the liquid. From the above considerations it is clear that in order that the possibilities of the instrument may be practically realised, temperature regulation constant to 1/50° is essential.

The dipping refractometer can be readily adapted for the measurement of the refractive indices of liquids obtainable only in small quantities. For this purpose the instrument can be easily converted into a modified type of Abbe instrument, a few drops of the liquid being applied to the face of an auxiliary prism which is then attached to the polished face of the refractometer prism, a film of the liquid interposing between the two prisms. The instrument can also be made "continuously reading" by the provision of a suitable vessel in which the prism is immersed, and through which the liquid flows.

The Interference Refractometer.

According to the wave theory of light, a ray of light is propagated through a medium termed the ether in the form of waves. The motion of the ether particles constituting the wave is transverse to the direction of propagation of the wave, this last requirement being introduced from a consideration of the phenomena of polarisation. Different colours, as developed in the spectrum, are characterised by differences in the nature of the waves by which they are propagated in the ether, the characteristics of a wave being its wave length, period and amplitude. The velocity of propagation of a disturbance in a medium is related to the wave length λ of the disturbance, and the periodic time T of the same, by the relation $v = \frac{\lambda}{T}$. Now if two trains of waves of identically the same characteristics are considered, emanating from two sources close to one another, it is clear that conditions can be adjusted so that at certain points a trough of the one wave train is superposed upon a crest due to the other train. Consideration of the case of waves propagated on water, lead immediately to the conclusion that under these circumstances any effect due to the one train of waves is annulled by the effect due to the other. In like manner points can be chosen in which crest is superposed upon crest, the result being an augmentation of the effect due to the single wave train at that point. Briefly, this is the basis of the doctrine of interference. In the case of light, the correspondence of the crest of the one train of waves with a trough due to the other, is marked by darkness, whereas where crest corresponds with crest or trough with trough, or put more generally, at any points

where the wave trains are superposed in the same phase, there is an augmentation of the effect due to each train, the augmentation being a maximum at the crest or trough of the system. One other theoretical point requires attention. A crucial experiment carried out by Fizeau showed that the relative refractive index of two media was equal to the ratio of the velocities of light in the media. It is clear, therefore, that if two trains of light waves with the same characteristics, emitted from the same source, pursue separate paths, a part of one path being constituted of a medium having a different refractive index from the uniform medium constituting the other path, then if later the two wave trains are superposed, the wave trains will no longer be in step,

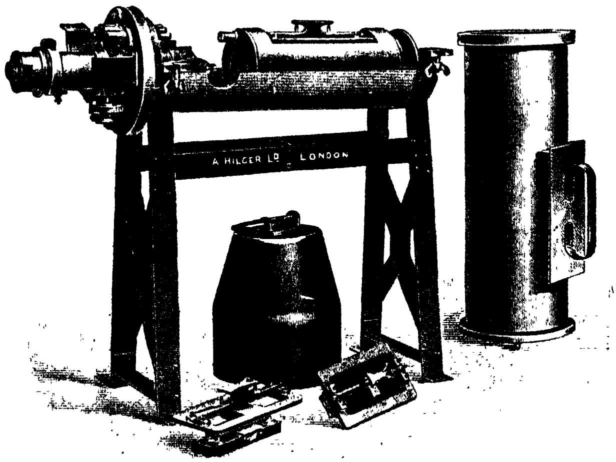


Fig. 100.

or "in phase," at all points on being superposed. This is the basis of the construction of numerous forms of interferometers. Of these, however, it is certain that few, if any, have up to the present satisfied the exacting demands of technological practice. A modified type of the Rayleigh interferometer[1] which has been devised for the determination of the refractive index of gases is of interest. In this instrument a very fine slit is illuminated by a bright source of white light. The light is collimated by a lens suitably placed in the collimating tube to which the slit is attached. The beam of collimated light is then divided into two, the separate beams pursuing parallel paths, each through a column of gas of any desired nature. Emerging from the columns of gas, the separate beams each traverse one of two fine slits, and the transmitted beams are superposed by a lens, being brought to a focus by means of the lens. A system of interference fringes results from the superposition of the beams, a difference of phase being introduced at some points by the beams having been propagated in

[1] *Collected Works*, Vol. IV., pp. 218, 364; *Roy. Soc. Proc.*, 1896, **59**, 198; 1898, **64**, 95.

media of different refractive index. Another set of fringes which may be termed the reference fringes is produced by the beams which pass over the tops of the tubes containing gas, and separately illuminate the fine slits mentioned. These two slits so illuminated form two sources emitting vibrations in the same phase, and the reference interference fringes arise from these slits being situated at different distances from any given point. The two sets of fringes so obtained are viewed by means of a cylindrical eye-piece—linear magnification alone being required—and by adjusting the pressure of the gas in one or other of the tubes, the bands are arranged so that the one set appears as the continuation of the other. This is achieved by

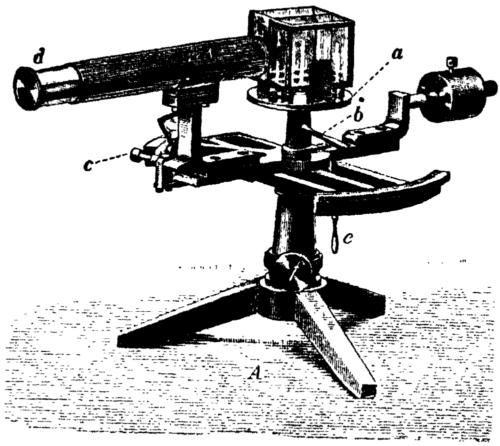


FIG. 101

identifying the central band of the system, this alone being free from colour, and arranging that the white band in each system is a continuation of the similar band in the other system. By varying the pressure of the gas in one of the tubes this adjustment is made, and the refractive index of the gas relative to that of the other is then determined. The necessary calculation is based upon the fact that for a gas $\frac{n-1}{\rho}$ or $(n-1)P$ is a constant, where P is the pressure, n the refractive index, and ρ the density of the gas. If the suffixes a and b refer to the two gases, when the adjustment is made as above, it follows that

$$\frac{n_a - 1}{n_b - 1} = \frac{P_b}{P_a}.$$

A type of interferometer suitable for technological work is illustrated in Fig. 100, p. 199.[1] Its general principle corresponds with what has been said above. The tubes may be used to contain either liquids or gases, and may be of length varying from 0·5 to 10 cm., and the accuracy in

[1] Made by Messrs Adam Hilger, Limited, Camden Road, London.

the measurement of refractivities varies accordingly from ·00006 to ·0000003. The two sets of interference fringes are brought into adjustment by altering the inclination of one of two glass plates interposed in the paths of the interfering beams. This change of inclination is measured by the rotation of a micrometer screw working at the end of the lever. The principle of auto-collimation is employed, the interference beams traversing the columns of liquid or gas once in each direction. Undue length of instrument is thus avoided. A small electric lamp forming an integral part of the instrument is used as the source of light.

Thornoe's Refractometer likewise utilises the principle of interference, and is especially useful in the analysis of beer.[1] It is illustrated in Fig. 101.

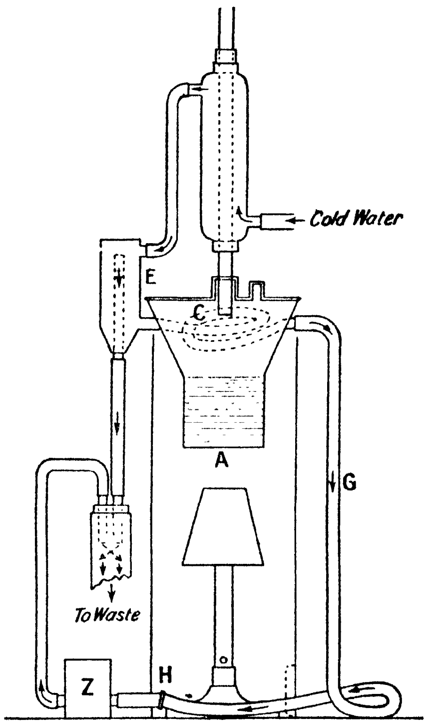


FIG. 102.

Temperature Control.

Some form of temperature control is in general necessary when using any form of refractometer in technical practice. In Fig. 102 is illustrated a simple thermostatic device due to Thorpe,[2] whereby a supply of tempered water at any predetermined temperature may be readily obtained and circulated in any desired part of the refractometric appliance. The vessel consists essentially of a vessel for generating steam or other appropriate vapour, containing a coil through which a current of water flows and is heated before it passes through the refractometer or other instrument, the position of which is shown at Z, by which the observations at a given constant temperature are to be made. The rate of flow of water is regulated by the screw clamp H. E is an arrangement for maintaining a constant head of water at the point of entrance to the coil. The apparatus is very readily brought into action, and under ordinary working conditions it is easily possible to secure a steady current of water not varying more than 0·1° or so in temperature throughout the day.

[1] *Cf.* Pope and Ling, *J. Soc. Chem. Ind.*, 1901, **20**, 735; also *Z. ges. Brauw.*, 1897, **20**, 373, 387.

[2] *J. Chem. Soc.*, 1904, **85**, 257.

POLARIMETRY—THE MEASUREMENT OF OPTICAL ROTATORY POWER

It is usual to specify the magnitude of the optical activity of a substance by what is termed the *Specific Rotation*. This varies with the wave length of the light employed, and is greater for light of short wave-length than for light of longer wave-length. It is the common practice to express specific rotation in terms of the D lines of the sodium spectrum, and so expressed, specific rotation is designated by the abbreviation $[\alpha]_D$. In the case of a pure substance the specific rotation is equal to the rotation produced by a length of 1 decimetre of the pure substance divided by the density. In the case of an active substance dissolved in an inactive solvent, the specific rotation is equal to the rotation produced by a decimetre of the solution divided by the weight of the active substance contained in 1 c.c. of the solution. Thus if α is the rotation produced with sodium light by a length l of the solution expressed in decimetres, d the density of the solution, and p the percentage concentration of the active substance, then :—

$$[\alpha]_D = \frac{\alpha}{l \times p \times d}.$$

It may be remarked that the specific rotation of a solution of an active substance depends not only upon the wave length of the light used, but also upon the concentration and temperature of the solution and the nature of the inactive solvent.

Light Sources.—Until recently the sodium lines were invariably used in technical polarimetry, and for many years any sodium source was considered suitable. Later the light filters of Lippich[1] and Landolt were introduced.[2] Subsequently, spectrum filtration was used. According to the Bureau of Standards,[3] the best results are obtained by feeding some form of fused sodium carbonate into an oxy-hydrogen flame. It is pointed out that noticeable variations in polariscopic measurements are likely to be observed with sodium sources at different intensities. The green line of incandescent mercury, $\lambda = 5461$ Å, is being more and more used for accurate polariscopic work. It is easily obtained by the use of a quartz mercury vapour lamp, combined with a prism of low dispersion. Lowry[4] suggests the following as suitable sources of light:—Lithium, 6708 red; cadmium, 6438 red; sodium, 5893 yellow; mercury, 5461 green; cadmium, 5086 green;

[1] *Z. Instrumentenk.*, 1892, **12**, 340.
[2] *Ber.*, 1894, **27**, 2872.
[3] *Circular* No. 44, 1918, p. 15.
[4] *Phil. Mag.*, 1909 [vi.], **18**, 320.

cadmium, 4800 blue; mercury, 4359 violet. The cadmium lines, he suggests, should be obtained from a rotating arc, using as electrodes an alloy of 28 per cent. cadmium, and 72 per cent. silver. For ordinary technological purposes a sufficiently intense sodium flame can be obtained by immersing a length of about three inches of thin sheet asbestos in a concentrated solution of common salt, drying, and then wrapping round the tube of an ordinary Bunsen burner, the asbestos forming a prolongation of the tube. The gas is lit at the asbestos.

FUNDAMENTAL PRINCIPLES OF POLARIMETRY

The simplest method of determining the plane of polarisation of a beam of plane-polarised light, is to pass the plane-polarised beam through a Nicol prism. When the Nicol prism is so orientated that its principal section is at right angles to the plane of polarisation of the light, no light passes through the prism, and complete darkness results. It is obvious that this principle can be applied to the construction of an instrument for the determination of the rotation of the plane of polarisation by passage of a beam through an optically active substance. Biot, in 1840, introduced the first polarimeter embodying this principle. It was soon found, however, that in actual practice such a system, while ideally simple, was very insensitive, the field of view appearing dark while the Nicol was rotated through quite an appreciable angle. The sensitiveness and accuracy of setting is very considerably increased in the modern polarimeter by utilising an auxiliary piece of apparatus, whereby the field of view is divided into two parts, and the light in these is polarised in planes inclined at a small angle to one another. It is obvious that when the analysing Nicol is turned so that its principal section is at right angles to the plane of polarisation in the one half of the field, that half will appear black. When turned so that the principal section is at right angles to the plane of polarisation in the *other* half of the field, *that* half appears black. If now the Nicol is turned so that its principal section is equally inclined to the respective planes of polarisation in the two halves of the field, the whole field will appear uniformly bright. It is obvious that the actual accuracy of setting should be proportional to the angle between the respective planes of polarisation, since rotation of the analysing Nicol through the angle changes the appearance of the field of vision from darkness in one half to darkness in the other. With a very small angle, however, the setting to equal illumination is a matter of difficulty, owing to the small amount of light from a given source then transmitted into either half of the field. On this account it is desirable to be able to adjust the sensitiveness of the instrument to the intensity of the source of light employed, as

it is obvious that with a feebler source of light a larger angle between the respective planes of polarisation in the two halves of the field must be employed. Devices whereby the light in the respective halves of the field is polarised in planes inclined at a small angle to one another will be referred to in the description of the various instruments.

Quartz Compensation.—More particularly in polarimeters used in the determination of sugar, and hence termed saccharimeters,

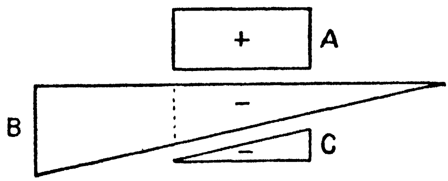


FIG. 103.

instead of actually measuring the angle of rotation of the plane of polarisation, this rotation is compensated by means of a counter rotation produced by a thickness, which can be conveniently varied, of some optically active material, more particularly quartz. Soleil found that the rotatory dispersion produced by solid rock crystal (quartz) and solutions of sucrose for various wave lengths were practically identical, and he introduced the system of quartz compensation into saccharimetry, which makes it possible to employ white light, the rotatory dispersion and consequent colour effect due to the solution of sucrose being negatived by the counter dispersion due to the quartz. The principle of quartz compensation will be readily understood from Fig. 103. The figure illustrates the single-wedge system of com-

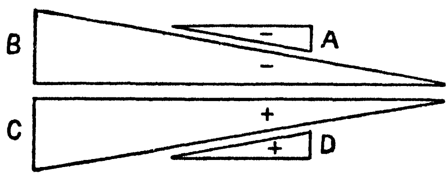


FIG. 104.

pensation. A is a plate of dextro-rotatory quartz and is stationary. C is a wedge of lævo-rotatory quartz and is likewise stationary. The wedge B of lævo-rotatory quartz can be moved laterally. In the position shown, the respective rotations impressed upon a beam of plane polarised light by the right- and left-handed quartz systems are equal, as the beam traverses equal thicknesses of the two kinds of quartz. This position is the zero position. The rotation produced by a dextro-rotatory sugar or other solution can evidently be com-

pensated by moving B to the right, when the beam traverses a greater thickness of lævo-rotatory quartz than of dextro-rotatory quartz. The system as figured is employed only to compensate for dextro-rotation. Lævo-rotation may be compensated by a similar arrangement in which dextro- and lævo-rotatory quartz are interchanged. The double-wedge system illustrated in Fig. 104 affords compensation for either dextro- or lævo-rotation. The wedges A and D of opposite rotation are fixed, while B and C similarly of opposite rotation are movable, so that any equivalent thickness of lævo- or dextro-rotatory quartz may be interposed in the path of the beam.

The application of the principles enunciated above will be shown by the consideration of a number of typical polarimeters.

The Duboscq Half-Shadow Polarimeter.

This instrument is illustrated in Fig. 105. The light from a sodium flame at L passes through a glass cell B containing a solution of potassium bichromate, which serves to deprive the light of blue and violet rays derived from the Bunsen flame. The rays are collimated by means of the lens C and fall upon a Jellett-Cornu prism P which is virtually

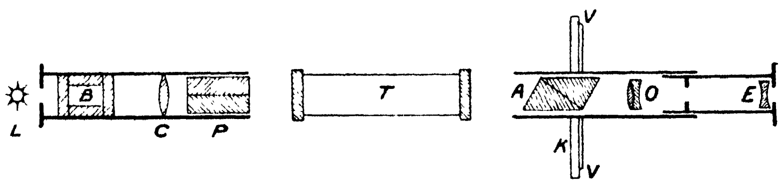


FIG. 105.—Duboscq Polarimeter.

an artificially twinned crystal of Iceland spar. It is produced by dividing an ordinary Nicol into halves along its whole length corresponding to the plane of the shortest diagonal. A small wedge of angle $\frac{\alpha}{2}$ is ground from the surface of both halves which are then re-united by means of Canada balsam. The transmitted beam of light consists of two portions of equal intensity polarised in planes inclined at an angle α to one another. T is the tube containing the optically active liquid. A is the analysing Nicol, and O and E together form a small Galilean telescope focussed on P. The analyser A is carried by a vernier VV moving over a fixed divided circle. One arm of the vernier reads directly degrees of rotation, the other, divisions of an arbitrary scale of which 100 divisions represent the rotation produced by 1 mm. of quartz.

Laurent's Saccharimeter.

This instrument again is of the half-shadow type, and is shown in section in Fig. 106. G is a lens used to concentrate the light from the sodium flame L on the aperture D, whence the light passes to the collimating lens C. Q is a half-wave plate of quartz cut parallel to the axis and covers one half the field of view of the instrument. It is of such thickness that it introduces a relative retardation of half a wave length of sodium light in the portion of the beam transmitted through it compared with that transmitted through the other half of the field. The result is that the beams occupying the respective halves of the field, although initially polarised in the same plane, are polarised, after transmission past or through Q, as the case may be, in planes inclined at an angle to one another. This angle is equal to twice the angle between the optic axis of the quartz crystal and

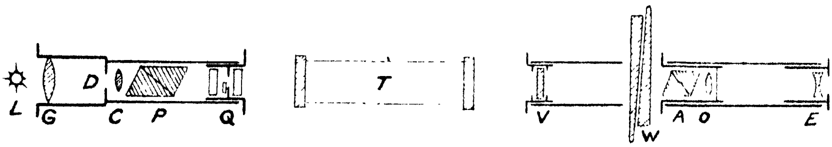


FIG. 106.—Laurent's Saccharimeter.

the original plane of polarisation of the beam. By means of a lever attached to P, this angle can be varied at will. When the angle is small the sensitiveness is great, but illumination of the field is weak. In any case, the maximum accuracy is obtained by employing an intense source of light at L, and the smallest half-shadow angle consistent with a distinctly visible field. The quartz plate V and wedges W are employed as quartz compensators in the manner already explained. The movable wedge carries a vernier, by which the amount of movement of the wedge necessary to restore uniform illumination of the two halves of the field on insertion of the optically active liquid in the tube T is read. The analyser A is mounted so as to be capable of a slight rotation, so that when the scale of the compensator is set at zero, A is rotated to the position such that the two halves of the field appear equally illuminated.

Soleil's Saccharimeter.

This instrument is shown in Fig. 107. The parts, L, C, T, V, W, O, E, serve the same purpose as in Laurent's Saccharimeter. The polariser and analyser P and A are double image prisms of Iceland spar achromatised by means of glass prisms. Q is what is termed a bi-quartz, and consists of two plates of quartz, one dextro-rotatory, the other

lævo-rotatory. They are cemented together so that each covers one half of the field of view. They are of such thickness that each rotates the mean yellow rays of the spectrum through 90°, so that when the principal sections of P and A are parallel, these rays are cut out, and the residual rays and blue rays form what is termed the sensitive or transition tint, which is complementary to the *jaune moyen* of Biot. The analyser is turned so that, using white light, the same tint of colour appears in each half of the field. With the slightest rotation of the analyser from this position, one half of the field appears red, the other blue. White light must be used with the instrument, and the sensitive tint can only be obtained with such light. In default of being able to use white light, or when the optically active liquid is appreciably coloured, recourse is had to the use of the quartz plate D

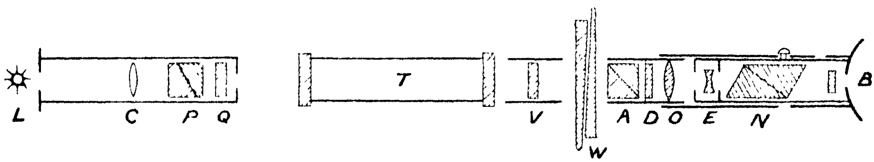
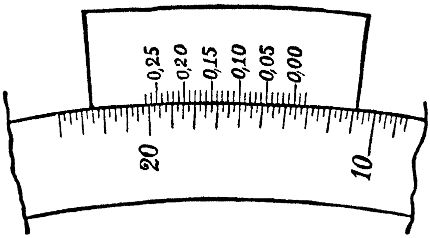


FIG. 107.—Soleil's Saccharimeter.

and the Nicol N. Rotatory dispersion of the light is produced in D and the orientation of N is adjusted so that the red and yellow rays are diminished in intensity, thereby restoring the sensitive tint. The Nicol N is protected from dust by the glass plate B. Soleil's instrument, it may be pointed out, is only suited for the examination of liquids such as solutions of sugar in which the rotatory dispersion, as has already been remarked, is the same as in quartz. Moreover, the rotation is measured for the mean yellow rays of wave length 0·00055 mm., whereas that of sodium light is about 0·00059 mm. The rotation measured with the Soleil instrument is generally designated $[\alpha]_j$. The Soleil instrument cannot be used by the colour blind, and the instrument is falling into disuse, in sugar technology, owing to the impossibility of employing the instrument with coloured solutions.

The Schmidt and Haensch Polarimeter.

The Schmidt and Haensch Polariscope is shown in Fig. 108, which also represents the general appearance of a polarimeter or saccharimeter. In the original form of polarimeters, the half-shadow device employed consisted of a Jellet-Cornu prism, details of which have been already given. In the later forms, the Lippich prism is more generally employed for this purpose. Otherwise the instrument introduces no new principle and is noteworthy principally on account



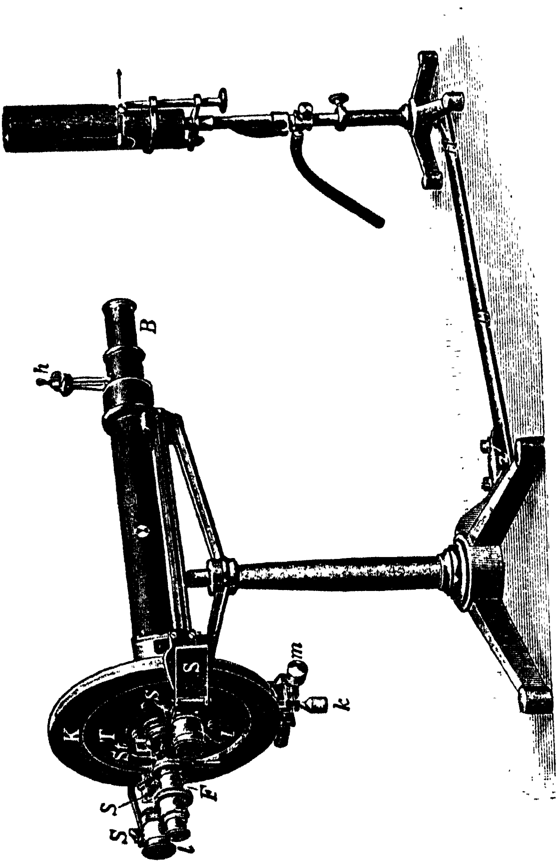


FIG. 108.

of mechanical refinements. The Lippich polarising system is accurate, and can be used with any kind of monochromatic light, and may be of the double or triple field type, and in the opinion of some, constitutes the only satisfactory method of obtaining a variable half-shadow angle.

The arrangement is shown in Fig. 109. The polariser is shown at P. B and C are two small prisms each of the same depth, but about half the width of the polariser. The small prisms are Lippich Nicols, while as polariser either a Lippich or Glan Thompson Nicol is used. These are slight modifications of the original type of Nicol prism. The small prisms have an angle of 93° at D and E, and about 87° at L and M, and the faces LD and ME are inclined at a small angle to the axis of the instrument, the edges D and E being parallel or nearly so.

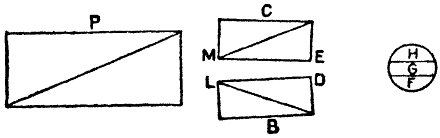


FIG. 109.

The eye-piece is focussed on these edges, and the field is seen divided by faint lines into three parts, F, G, and H (see figure), or two if D and E are in contact. If the system is viewed through an analyser whose principal section is at right angles to that of P, G appears relatively darker than F and H. When the analyser is turned so that its principal section is perpendicular to those of B and C, G appears relatively brighter than F and H. The adjustment is therefore made by oscillating the analyser between these two positions, gradually decreasing the angle of oscillation until equality of the three fields F, G, and H is secured.

Determination of Optical Rotatory Power.

Reverting to the figure of the Schmidt and Haensch instrument (Fig. 108), the following description will indicate the general method of determining the optical rotatory power of any liquid with the appropriate type of polarimeter. F is the telescope, *l*, *l*, lenses for reading the verniers moving over the sliding scale K of the instrument. The analysing Nicol is at *St* and moves with the telescope and revolving graduated dial; *h* represents the movable polariser, with the graduated segment of a circle fixed to it. B contains bichromate solution. A sodium flame is employed with the instrument. The graduated dial is made to revolve by means of *St* by hand, or by a micrometer screw *m*, after the screw head *k* has been fixed. The dial is, as a rule, graduated all the way round. In addition to whole degrees, half and quarter degrees are indicated on the dial. By means of a vernier the scale is read to 0·01°. If desired, a second scale graduated to read directly sugar percentages is provided. The instrument being directed towards the brightest part of the sodium flame, the zero position is found by focussing the telescope on the

Lippich polariser, so that the field presents a perfectly clear round circle divided into two equal parts by a sharply-defined vertical line. If the graduated dial is turned through three or four degrees to the right or left, one half of the field becomes brighter, the other darker. The zero position is adjusted so that the zero line of the circle coincides with the zero of the vernier. The sensitiveness of the instrument is adjustable by means of *h*. When *h* is in its zero position, and at the same time the analyser A is placed in the zero position, both halves of the field appear black. The instrument is the more sensitive the more nearly *h* is adjusted to the zero position. As already explained, however, the minimum of light is available in such a position, and in general the position of the pointer at $7\frac{1}{2}°$ is most suitable particularly when the solutions are not quite transparent. When the pointer is moved, the zero point of the instrument changes and no longer corresponds with the zero line of the dial. The difference between the latter and the zero position must either be taken into account (the simpler way) or else, after the graduated dial has been moved to zero, the apparatus must be again placed in the zero position. To do this the analysing Nicol is turned by means of a screw until the half shadows present the same appearance.

Special attention must be paid to the following point, which if not noted may lead to considerable confusion. When the circle has been turned too far, and has gone beyond the sensitive range of the apparatus, the light, on comparison, appears of the same intensity on either side of the dividing line, and the point may be mistaken for the zero position. Under these circumstances the circle may be turned through 10, 15, or 20° or so with hardly any change in the appearance of the respective halves of the field. It is particularly necessary, therefore, to see that in determining the zero position and subsequent reading with the active substance that the transition from light to shade and *vice versa* occurs abruptly on rotating the dial.

To determine the rotation produced by the optically active solution, the sample is placed in the tube and the circle turned until the two halves of the field present the same appearance. The rotation is then read off from the graduated dial. In an instrument provided with quartz compensation, the equivalent rotation is read by adjusting the quartz compensation device so that equality of the two halves of the field is secured as already explained, and the reading indicated by the scale attached to the device taken.

Numerous mechanical and optical improvements have been introduced by makers of polarimeters in recent years. Thus Bellingham and Stanley secure greater illumination of the scale by constructing this so that it faces the source of light. The polariser and analyser, moreover, are optically stable. They employ quartz wedges only

20 mm. long, whereby the selection of better optical specimens becomes possible. Accuracy of reading is secured by means of a vernier of special design.

Polarimeter Tubes.—The liquid to be examined for optical rotatory power is contained in a tube of the form shown in Fig. 110. It will be noticed that one end is considerably wider than the other. With a tube of this form, any air bubbles in the liquid collect at *a*

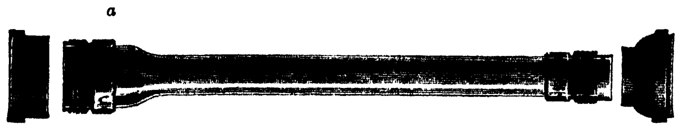


FIG. 110.

and are thus outside the field of vision. The tube is provided with ground ends which fit against plane glass plates. The glass tube is fixed into metal end pieces provided with screw caps and india-rubber washers by which the plates of glass can be screwed down firmly against the respective ends of the glass tubes. Care must be taken that the pressure so introduced does not render the glass plates doubly refracting. The absence of double refraction is tested by placing the tubes in position when empty with the ends screwed tight. The tubes are generally some multiple of 10 cm. in length, the

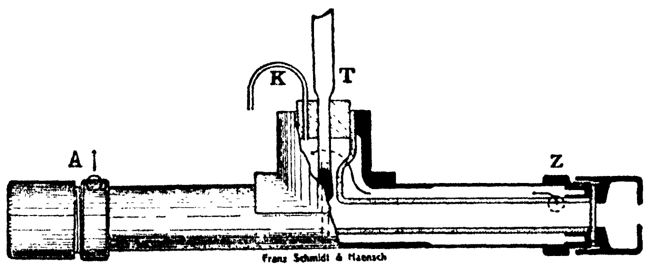


FIG. 111.

appropriate value being marked on them. Their exact length can be ascertained if desired by means of a suitable gauge. The employment of tubes of different lengths enables one to decide upon the actual rotation, when the direction of rotation is unknown or when the rotation is considerable. In Fig. 111 is shown in section a water jacketed tube, whereby the temperature of the liquid may be effectively controlled. The active liquid is introduced by way of the funnel-shaped projection which also serves for the insertion of a thermometer T as shown. Care must be taken that the thermometer does not project into the tube so as to obscure the

field of vision. Tempered water derived from a device such as that shown in Fig. 102 is circulated through the jacket.

Special types of polarimeter tubes have been designed by Bates, Landolt, Pellet, Yoder, and Wiley. For particulars of these see *Circular* 44, *Bureau of Standards*, Washington, 1918.

Control Tube for checking the Scale of the Saccharimeter.—For purposes of checking the scale of a saccharimeter a telescopic form of control tube whose length can be adjusted either from 0 to 210 mm. or from 210 to 420 mm. is commonly employed. This tube, due to Landolt, as manufactured by Schmidt and Haensch, is shown in Fig. 112. The tube is employed in the following manner:—A sugar solution is prepared of such strength that it gives a reading of 100 divisions at a length of about 400 mm. The tube is filled by removing the funnel which serves to receive the overflow of solution as the tube is shortened, and closing the opening by means of a plug.

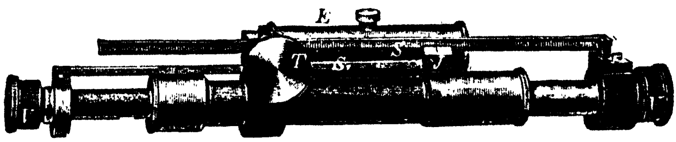


FIG. 112.

The tube is drawn out to its full extent, and after removing one of the caps, filled in the usual way. The scale readings corresponding to various lengths of tube are then ascertained in the usual manner and compared with the calculated values. Further particulars will be found in *The Optical Rotatory Power of Organic Substances* by Landolt, 1902, p. 441.

In verifying a saccharimeter by means of sucrose solutions, it is important to bear in mind the variation of the specific rotatory power of the sugar with concentration. The table calculated by Browne from the experiments of Schmidt and of Landolt is useful in this connection.[1]

Details of the various saccharimeter scales employed in practice are given in the section on Sugar (Vol. VI.).

Effect of Temperature.—For the ordinary polarimeter employed for measuring absolute rotations, no temperature correction other than that necessary to allow for any zero-shift that may occur is necessary. In instruments employing a quartz wedge for neutralising the rotation of the substance, a temperature correction is unavoidable. Schönrock[2] has pointed out that the necessary correction is made up of three parts: (1) a correction due to change in shape of the quartz wedges; (2) that due to a change in the specific rotation of quartz with

[1] *Handbook of Sugar Analysis*, 1912, p. 118. [2] *Z. Ver. deut. Zuckerind.*, 54, 521.

temperature; and (3) the change due to the expansion or contraction of the material of the scale.

It can be shown[1] that for quartz-compensating saccharimeters having a scale engraved on nickeline, that the scale reading S_t and t° is related to the required scale reading at 20° by the equation:—

$$S_{20} = S_t\{1 + 0.000148(t - 20)\}.$$

When the scale is etched on the quartz wedge the correction coefficient is 0·00013.

The influence of temperature on the specific rotation of sucrose has been studied by numerous investigators. Schönrock gives:—

$$[\alpha]_D^t = [\alpha]_D^{20} - [\alpha]_D^{20}\, 0.000217(t - 20).$$

He also found for the normal sugar solutions that the temperature coefficient was independent of the wave length of the light employed, but that it decreased with increase in temperature, thus:—

Temperature.	Coefficient.
10°	0·000242
20	0·000184
30	0·000121

In the ordinary testing of sucrose, the solution is made up to volume and read at the same temperature, which, in general, is not the standardisation temperature. It is desirable, therefore, to know the variation in the saccharimeter reading of an approximately normal sucrose solution per 1°. The results obtained by different observers are as follows:—

Andrews[2]	0·0300
U.S. Coast and Geodetic Survey	0·0293
Wiley[3]	0·0314
Prinsen Geerligs[4]	0·0300
Watts & Tempany[5]	0·0310
Mean	0·0303

The value obtained by adding together the best values of the separate coefficients entering into this constant is 0·0348. The polarisation in sugar degrees at 20° (V_{20}) of an approximately normal sucrose solution made up and measured at the same temperature t° is thus given by:—

$$V_{20} = V_t\{1 + 0.0003(t - 20)\}$$

and this is sufficiently accurate for all ordinary polarimeter measure-

[1] *Circular No.* 44, *Bureau of Standards*, 1918, p. 37.
[2] *Technology Quarterly*, Massachusetts Institute of Technology, May 1889, p. 367.
[3] *J. Amer. Chem. Soc.*, 1899, **21**, 568.
[4] *Archief. Java. Suikerind.*, July 1903.
[5] *West Indian Bulletin*, vol. iii., p. 140.

ments whatever be the type of tube or scale. If, however, the solution be made up to volume at 20°, while the polarimeter measurement is made at another temperature, all apparatus being at this temperature, the above formula is no longer applicable. Under these circumstances the formula [1] to be applied is :—

$$W_{20} = W_t\{1 + 0.000609(t - 20)\}.$$

Clarification.—For polarimetric purposes active solutions frequently require clarification. The clarifying agents most commonly employed include: (1) alumina cream; (2) basic lead acetate; (3) animal charcoal. Others possessing advantages in special cases are: (4) neutral lead acetate; (5) basic lead nitrate; (6) alum solution; (7) sodium hyposulphite; (8) sodium hypochlorite. Particulars relative to these various clarifying agents will be found on pp. 63-73 of *Circular* 44, *Bureau of Standards*, Washington, 1918.

Basic lead acetate solution is prepared by Ling in the following manner: 150 g. of fine lead acetate crystals is mixed in an evaporating basin with 45 g. of litharge and 25 c.c. of water. This paste is allowed to remain at room temperature for two to three hours with frequent stirring. The paste is then gently warmed on a piece of wire gauze or sand bath, and then poured into 500 c.c. of water, and allowed to stand until the small amount of undissolved sediment settles out. The solution is then filtered, and the sp. gr. of the clear filtrate should be 1·20.

Alumina cream is made by pouring a cold 2 to 3 per cent. solution of alum into dilute ammonia of sp. gr. 0·98, in a bottle. The alumina is allowed to settle, and washed in the bottle by decantation twice a day until the supernatant liquid gives no reaction with barium chloride. This usually takes a week.

In conclusion, it may be mentioned that the polarimeter finds increasing use in the determination of sugar, starch, essential oils, the examination of alkaloids, camphors, lubricating and mineral oils, etc. Its use is not necessarily confined to the determination of optically active substances; a large number of inert substances exert a powerful influence on the rotatory power of active solutions. As an example of such application it may be mentioned that acetone and boric acid can be determined by this means in solutions of tartaric acid of known strength. Moreover, the solvent used to dissolve an optically active substance exercises considerable influence on the activity of the solution, and this fact may afford a considerably widened field for the use of the polarimeter in technical practice.

[1] *Circular No.* 44, *Bureau of Standards*, Washington, 1918, p. 39.

THE MEASUREMENT OF ELECTRICAL CONDUCTIVITY

The resistance of an electrical conductor is defined in accordance with Ohm's Law as the constant of proportionality between the difference of potential at the ends of the conductor to the current flowing in the conductor. Thus if a current C amperes flows in a conductor when a difference of potential or voltage, or electromotive force, as it is indifferently termed, equal to E volts, is established between the ends of the conductor, then the resistance of the conductor is equal to R ohms, where R is given by the relation $R=\frac{E}{C}$, and in accordance with Ohm's Law the value of R is a constant for any

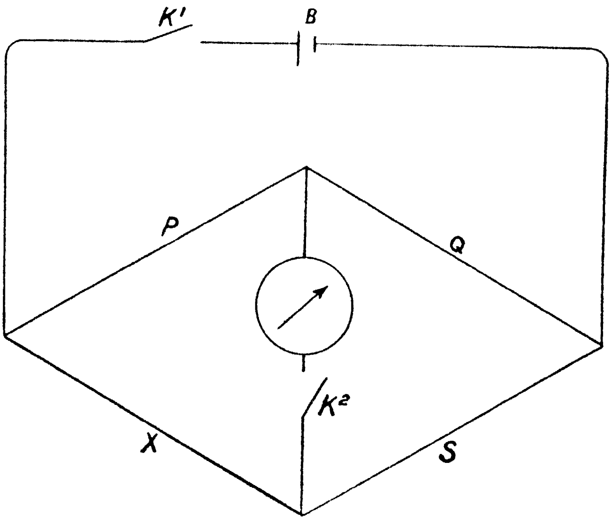


FIG. 113.

given conductor, independent of the value of the difference of potential applied to the ends of the conductor, provided the temperature and physical state of the conductor are unaltered.

The methods for the measurement of the resistances of solid conductors are detailed in any text-book of Practical Physics (see, for instance, Watson's *Text-book of Practical Physics*, Longmans, 1913, pp. 432-474). The most commonly employed method depends upon the use of the Wheatstone bridge in one of its many forms. It must here suffice to say that the Wheatstone bridge consists of four resistances, X, P, Q, and S, connected as shown in the diagram, Fig. 113. A battery B is connected with the arms of the bridge via the key K^1, and a galvanometer G via a second key K_2, and the various resistances

X, P, Q, and S being adjusted so that on depressing K_1 and then K_2 and maintaining both keys depressed (it is important that the keys be depressed in the order specified) no deflection of the galvanometer is produced, the elementary theory of the bridge shows that under these conditions $X = \frac{P}{Q}.S$. The common practice is to adjust P and Q to any desired values—say $P = 1$, $Q = 1000$ ohms—and then vary the resistance S until balance of the bridge is achieved. During the preliminary adjustment of S to the required amount, the sensitiveness of the galvanometer is suitably reduced by shunting it with an appropriate resistance, so that no large deflections of the galvanometer are produced. The full sensitiveness of the galvanometer need only be employed in making the final adjustments to balance. The resistance of the conductor, however obtained, is measured in terms of the ohm as a unit.

It is customary to speak of the resistance of a conductor in terms of what is called its *specific resistance.* This is defined as being equal to the resistance of a cube of the substance of 1 cm. side, the current passing through the cube normally from one face to that opposite. It follows immediately that the resistance R of a specimen of the conductor of length L cms., and cross-section A cms., is related to the specific resistance of the specimen by the relation $R = \rho \frac{l}{A}$. It will be seen that the appropriate unit for the designation of specific resistance is the ohm-cm. More especially when considering the electrical properties of solutions, it is customary to speak of the *specific conductivity* of the conductor or solution. The specific conductivity σ is the inverse of the specific resistance ρ, thus $\sigma = \frac{1}{\rho}$, and the appropriate unit for the designation of specific conductivity is the ohm^{-1} $cm.^{-1}$. The unit of conductivity is indifferently referred to as the reciprocal ohm or mho.

In chemical technology, occasion most frequently arises for the measurement of the specific conductivity of solutions, and this operation will alone be considered in the present section. While the method of the Wheatstone bridge is applicable to such measurements, the use of direct currents is rendered difficult owing to polarisation effects at the electrodes inserted into the solution. Owing to the existence of these polarisation effects, the current through the electrolyte is not, in general, proportional to the E.M.F. applied to the electrodes. A back E.M.F. due to polarisation is produced at the electrodes.

The phenomena of polarisation as influencing the measurement of the conductivity of a solution have been examined in great detail

by Kohlrausch, who has shown how the effects of polarisation may be obviated by the use of an alternating current in a special type of Wheatstone bridge, a telephone being employed in place of the

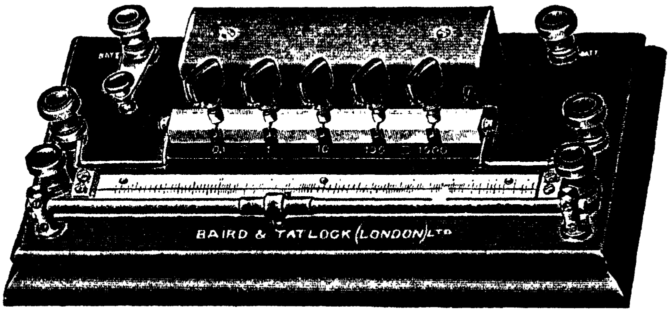


FIG. 114.

galvanometer customarily used. This type of bridge is illustrated in Fig. 114. The bridge is represented diagrammatically in Fig. 115. The four arms of the bridge are constituted respectively of the resistances X to be measured, inserted between the terminals A and C, the

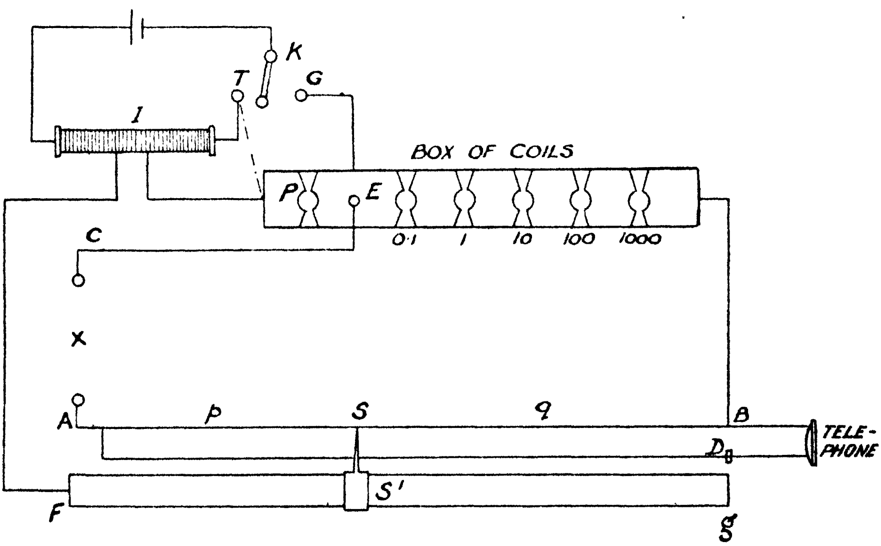


FIG. 115.

resistances unplugged in the box of coils shown, and the two portions of the bridge wire AS and BS into which the bridge wire is divided at the point of contact of the slider S. The Kohlrausch Universal bridge is so constituted that it can be used either with alternating

or direct current, the latter being employed when ordinary measurements of conductors are being made. For use with alternating currents, the current in the bridge is derived from the secondary coil of a small induction coil whose primary terminals are connected with a two-volt accumulator or two Daniell cells. For use with alternating current, the key K is turned so as to make contact with the stud T, the plug P being inserted. For use with direct current and a galvanometer, the key K is depressed to make contact with the stud G, and the plug P removed. The telephone is connected to the ends of the wire AB as shown, one terminal being connected to B and the other to A by means of the rod AD. The terminals of the secondary of the induction coil are brought to E and S. The slider S^1 slides along the rod FG, so that contact can be made at any point S on the wire AB. Although every sample of telephone is not equally suitable for use with the bridge, common telephones are frequently found satisfactory. It is a convenience to use two such telephones, attached to a light spring which rests upon the observer's head, one telephone resting against each ear. The coils in the box are composed of resistances 0·1, 1, 10, 100, and 1000 ohms, and the bridge is suitable for resistance measurements between 0·05 and 20,000 ohms with sufficient accuracy for most technical purposes. In general it is found that no position of the slider S^1 is possible, so that the sound in telephone is reduced to zero. This absence of a position of zero noise is attributable to the existence of self-inductance and capacity effects in the bridge. Chaperon[1] has shown that the disturbance is mainly attributable to the capacity effect of the coils, and has devised a means of winding the coils so as to reduce it to a minimum. The practice in using the bridge consists in determining the position of the slider S^1 so that the noise in the telephone is reduced to a minimum. This position is best located by oscillating the slider from side to side of the approximate position of this point so that equal loudness of the noise in the telephone is heard. The amplitude of the motion is gradually and continuously reduced until finally the position of the minimum is located as accurately as possible. The experiment is repeated a number of times and the mean of the various readings of the slider taken. If the balance point S divides the wire AB in the ratio $\frac{p}{q}$ then the resistance of $X = \frac{p}{q}$ (resistance unplugged from box). For greater accuracy, the coil which brings the point of balance on the wire as near to the middle as possible should be unplugged from the box. The scale of the bridge is graduated so as to indicate the ratio $\frac{p}{q}$ directly. The induction coil employed may constitute an integral part of the apparatus or any other coil

[1] *Comptes rend.*, 1889, **108**, 799.

may be inserted in the bridge. The coil employed should make very little noise. If one ear alone is used with the telephone, it is well to plug the other with cotton-wool. The coil may, if found desirable, be placed outside the room or encased in cotton-wool and surrounded by a box.

Preparation of the Solution of the Electrolyte.

The preparation of the solution of the electrolyte demands considerable attention, more particularly when dilute aqueous solutions are being investigated. According to Kohlrausch and Heydweiller, the specific conductivity of the *purest water* obtainable in a vacuum is $0{\cdot}04 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. That of what is termed *Conductivity water* in air at 18° is about 10^{-6} (ohm cm.)$^{-1}$, a twenty-five fold increase. The specific conductivity of a $N/1000$ solution of potassium chloride at 18° is approximately $0{\cdot}00012$ (ohm cm.)$^{-1}$ = 120×10^{-6} (ohm cm.)$^{-1}$, *i.e.*, 120 times greater than that of conductivity water. For the ordinary measurements of electrolytic resistances in chemical technology particularly when dilute solutions are being investigated, satisfactory water may be prepared from ordinary distilled water in the following manner. Some distilled water is placed in a carefully cleaned beaker and boiled. The beaker is emptied and a fresh supply placed in the beaker, which is then immersed in a freezing mixture. The beaker is not stirred. A coating of ice forms round the walls of the beaker. When about a quarter of the water has frozen, the remaining water is thrown away and the ice melted. The water obtained on melting ice possesses a much smaller conductivity than the original distilled water. It should be used at once and not stored, as it dissolves salts from the glass vessels in which it is kept. The amount of salts so dissolved depends upon the nature of the glass vessels employed. A variety of glass particularly resistant to the action of water was originally introduced by Schott & Co., of Jena. Vessels made of glass of equal, if not superior, resistant qualities are now manufactured by a number of firms in England and elsewhere. Vessels made of such glass should alone be employed to contain liquids whose electric conductivity is to be determined, and the liquid should, moreover, not be contained in or transferred to vessels of any other kind of glass prior to, or during, the experiment. Conductivity water when required may be prepared by the methods detailed by Bousfield,[1] Hartley, Campbell and Poole,[2] Thole[3] and others.

[1] *J. Chem. Soc.*, 1905, **87**, 704 ; 1912, **101**, 1443.
[2] *J. Chem. Soc.*, 1908, **93**, 428.
[3] *J. Chem. Soc.*, 1912, **101**, 207.

Method of Platinising Electrodes.

In the measurement of electrolytic conductivities, platinum electrodes are frequently employed, and it is essential that these should be platinised, as thereby polarisation effects are considerably reduced. For this purpose, the platinum electrodes are carefully cleaned and placed in a solution containing three parts of platinic chloride, 0·025 part of lead acetate, and 100 parts of water. A current is passed through the solution, the current strength being adjusted so that a free and regular evolution of bubbles occurs, and an adhesive deposit of platinum black is obtained. The current in the solution is reversed from time to time. The electrodes after removal from the solution are well washed with water, and are then allowed to stand in distilled water for some hours. It may be remarked that re-platinising the electrodes usually remedies the defect of the position of the minimum noise in the bridge becoming rather indefinite.

Absolute Measurement of Specific Conductivity of an Electrolyte.

When the absolute specific conductivity of an electrolyte is to be determined, the liquid is best contained in a vessel of the form shown in Fig. 116. This electrolytic vessel consists of two stout-walled test tubes or bottles fitted with side tubulures as shown. The tube B is inserted through the tubulures through corks of wood or indiarubber,

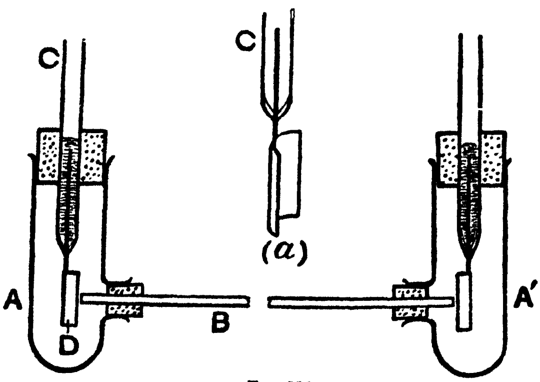


FIG. 116.

or may, if desirable, be fused on to the vessels A and A′. Each electrode consists of a plate of platinum welded to a short length of platinum wire which is fused into a piece of glass tubing. Mercury is poured into the tubing to effect contact between the electrodes and the rest of the bridge, wires being dipped into the mercury for this purpose. The glass tubes pass out through corks, as shown,

which serve to hold the electrodes in position. The electrodes are platinised as described above. The tube B consists of a fairly short and wide-bored tube, such that the resistance of the liquid therein is about 500 ohms. The diameter of the tube is ascertained by weighing the tube empty and then filling with water, the ends being corked with plane-ended corks. The diameter of the tube is found by employing the formula $d = \sqrt{\frac{4W}{\pi \rho l}}$ where W is the weight of the water, d the diameter of the tube, l length of water column, and ρ density of water at temperature of experiment. The electrolytic solution to be examined is introduced into the tubes A, A′, and B so as to cover the electrodes completely, and so that no air bubble is present in the tube B. The vessel is immersed in a bath at constant temperature and the resistance measured as already described, employing the Kohlrausch bridge. The specific conductivity of the solution is given by $\rho = \frac{\pi d^2 R}{4l}$ where l = length of the tube B, d its diameter, and R the measured resistance.

Comparison of Specific Resistances.

Most frequently in chemical technology, and indeed for chemical purposes in general, occasion arises for the comparison of the specific conductivities of two or more solutions. If one of the solutions

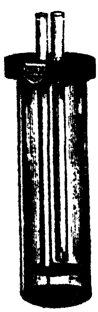


Fig. 117.

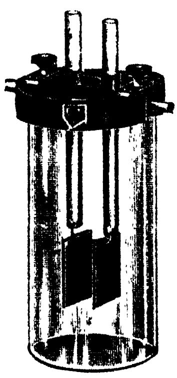


Fig. 118.

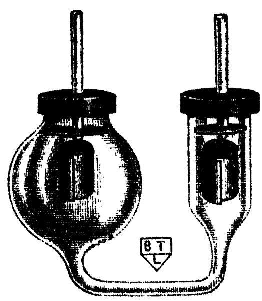


Fig. 119.

Fig. 120.

Fig. 121.

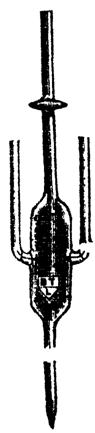


Fig. 122.

employed is a solution whose specific conductivity at the temperature of the experiment is accurately known, the comparison enables the specific conductivity of the other solution to be calculated. For this purpose various forms of vessels to contain the solutions in turn are available. A selection is shown in Figs. 117-122. Whatever form of

vessel is chosen, it should be constructed of glass highly resistant to the solvent action of the solution. The electrodes, if of platinum, should be platinised as already described, and should be removable for cleaning purposes. The form of vessel shown in Fig. 118 is especially applicable to the determination of the change of resistance with temperature of badly conducting solutions, a thermometer being inserted into the electrolyte to indicate its temperature when cooling. The form shown in Figs. 120 and 121 can be introduced within the liquid contained in a beaker, etc., and subject to the condition that the liquid stands in the outer vessel at a higher level than the upper orifice, affording entrance of liquid to the vessel: the resistance is independent of the quantity of liquid in the outer vessel. The form Fig. 120 is used for bad conductors, the form Fig. 121 for good conductors. The pipette form shown in Fig. 122 enables the liquid under investigation to be readily sucked up into the space between the electrodes and retained there. The constant of the vessel, as it is termed, is found by first measuring the conductivity or resistance of a solution of known specific conductivity in the vessel, and thereafter carrying out a similar measurement, using the liquid under investigation in the vessel. Thus, if K_0 is the measured conductivity of a liquid of known specific conductivity k_0 contained in the vessel, the specific conductivity k_1 of a liquid, the measured conductivity of which when contained in the vessel is found to be K_1 is given by $k_1 = \frac{k_0}{K_0} . K_1$. The factor $\frac{k_0}{K_0}$ obviously is such that multiplying the observed conductivity K^1 of the liquid by it reduces the observed conductivity K^1 to the desired specific conductivity k_1. It is termed by Kohlrausch the *resistance constant* of the cell. For purposes of standardising the vessel, the best solution to employ is a solution of pure potassium chloride. It may be remarked here (the matter is illustrated in the table below) that the specific conductivity of a solution is dependent upon the temperature, and consequently it is of importance that the temperature be maintained constant during an experiment.

Specific Conductivity of Certain Solutions and the Variations of same with Temperature.

The following table contains particulars of the specific conductivities of solutions of certain electrolytes at various temperatures.[1] These can be employed for calibrating the vessels described above. The solutions specified are prepared as follows:—

(1) Solution of sulphuric acid of maximum conductivity at 18°.

[1] Kohlrausch, Holborn, and Dieselhorst, 1898.

Dissolve 378 g. of ordinary concentrated H_2SO_4 (97 per cent. H_2SO_4) in distilled water and dilute to one litre at 18°.

(2) Solution of magnesium sulphate of maximum conductivity at 18° C. Dissolve 552 g. of dry magnesium sulphate ($MgSO_4, 7H_2O$) in one litre of water.

(3) Solution of sodium chloride, saturated at 18° and at all other temperatures. Shake an excess of sodium chloride with distilled water (about 450 g. of salt per litre) and filter.

(4) Normal solution of potassium chloride. Dissolve 74·555 g. of potassium chloride in water and dilute to one litre. The more dilute solutions are obtained therefrom by suitable dilution.

Temperature, °C.	Specific Conductivity of Solution of:—						
	H_2SO_4 of maximum conductivity at 18°.	$MgSO_4$ of maximum conductivity of 18°.	Sodium Chloride saturated.	Potassium Chloride.			
				N	$\frac{N}{10}$	$\frac{N}{50}$	$\frac{N}{100}$
	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}	ohm^{-1} cm^{-1}
0	0·5184	0·02877	0·1345	0·06541	0·00715	0·001521	0·000776
5	0·5792	0·03402	0·1555	0·07414	0·00822	0·001752	0·000896
10	0·6408	0·03963	0·1779	0·08319	0·00933	0·001994	0·001020
15	0·7028	0·04555	0·20146	0·09252	0·01048	0·002243	0·001147
18	0·7398	0·04922	0·21605	0·09822	0·01119	0·002397	0·001225
20	0·7645	0·05171	0·22596	0·10207	0·01167	0·002501	0·001278
25	0·8257	0·05808	0·2513	0·11180	0·01288	0·002765	0·001413
30	0·8860	0·06459	0·2774	...	0·01412	0·003036	0·001552
35	0·9453	0·07121	0·3041	...	0·01539	0·003312	...

A table containing particulars of the specific conductivity, and other characteristics of a large number of electrolytic solutions, has been drawn up by Fitzpatrick.[1] It will be seen from the above table that the specific conductivity of an electrolyte *increases* with increase of temperature. In general, the value of the temperature coefficient, *i.e.*, the value of $\frac{1}{k_{18}}\left(\frac{dk}{dt}\right)$ is of the order of about 2 per cent. per degree.

COEFFICIENT OF IONISATION AND IONIC VELOCITIES. ELECTROMETRIC TITRATION

The specific conductivity of a solution may be regarded as made up of two parts, viz., that due to the kation and that due to the anion in solution. Regarded from this point of view, it can be shown that the specific conductivity of a dilute solution is equal to:—

$$\alpha N n \epsilon_0 (u_0 + v_0)$$

where α is the coefficient of ionisation of the electrolyte, *i.e.*, the fraction

[1] Cf. *Brit. Assoc. Report*, 1893.

of the total number of molecules of the electrolyte which become ionised on solution, N the number of gram molecules of the solute dissolved per c.c. of solution, n is the valency of the ions in solution, ϵ_0 is the electric charge carried by a gram molecule of the solute (96,550 couloumbs) and u_0 and v_0 are the respective velocities of the kation and anion under unit potential gradient. In the case of a compound such as K_xA_y in which K is γ-valent, and A is β-valent, $n = \gamma x = \beta y$.

In any application of the measurement of electrolytic conductivity to the determination of the concentration of the electrolyte in the solution, it must be borne in mind that α, u_0, and v_0 are themselves dependent upon the concentration and temperature of the solution. They may be regarded as approximately constant in dilute solution at constant temperature. Where, however, solutions of the same electrolyte of markedly different concentrations are to be compared, the respective values of α, u_0, v_0 must be employed before the ratio of the concentrations of the electrolyte can be accurately determined from the observed ratio of the specific conductivities.

The measurement of electrolytic conductivity is of general application in chemical technology. When pure substances are in question, the method affords a ready method for the comparison of the respective concentrations of two solutions of the same substance. Considerable caution is, however, necessary where the method is to be applied to the determination of the concentration of impure substances. The presence of small proportions of $\overset{+}{H}$-ion or of $\overset{-}{OH}$-ions may influence the conductivity of the solution considerably. They are respectively the kation and anion possessing the highest ionic velocities under unit potential gradient.

The method has been applied by Main[1] to the determination of the ash content of sugars and syrups. The electrical conductivity of a solution of the sugar or syrup is attributed to the presence of salts which when in solution in water yield a conducting solution. If the relative proportion of the various salts present is constant, a determination of the electrical conductivity of a solution of definite strength should enable the approximate amount of such salts present to be determined. Main found that the resistance of his solutions was inversely proportional to the ash content of the sugar or syrup, this latter being determined gravimetrically. The method has been further examined by Lange,[2] who finds that it is reliable provided that the ash contents of the sugars compared do not differ by more than 0·5 per cent.; he has prepared tables for the electrical con-

[1] *Seventh Int. Congress of Applied Chemistry*, 1909, p. 334.
[2] *Z. Ver. deut. Zuckerind.*, 1910, **60**, 359-381.

ductivity of sugar solutions for sugars containing up to 3 per cent. of ash. Work on the same subject has been done by Reichert[1] and Landolt.[2]

Dutoit[3] and his collaborators have employed the measurement of electrolytic conductivity for ascertaining the end point in volumetric reactions. The solution to be tested should be very dilute ($N/100$-$N/200$) and the precipitating or otherwise reacting solution comparatively strong ($N/1$). The end point is marked by a point of inflexion in the curve obtained by plotting the conductivity of the solution against the volume of precipitating solution added. The method has been modified so that the potentials of the solution against an electrode are plotted, as ordinates, against the amount of precipitant added, as abscissæ. A sharp double inflexion marks the end point. The method is especially applicable to the determination of iodine in urine, and the estimation of small quantities of chlorides in chlorates.

Van Suchtelen and Itano[4] have examined the precision of the conductivity method of titration in the cases of the titration of solutions containing Cl, Ag, SO_4, Ba, U, PO_4, NO_3, K, Ca, and Fe. These ions are all readily determined by the method. The results are not affected by the presence of foreign substances, and it is found possible to determine more than one substance in the same solution by a suitable choice of reagent, Cl and SO_4, for example, being titrated with silver nitrate and barium nitrate respectively. Ziegel[5] has described a device by means of which the change of potential occurring in a solution at the end point of a titration is utilised for automatically closing the stopcock of the burette when the end point is reached. A similar apparatus has been described by Forbes and Bartlett.[6]

Harned and Laird[7] have employed the measurement of electrical conductivity for the titration of oxalic acid. A sharp change in the direction of the curve obtained by plotting the value of the electrical conductivity against the amount of added alkali is obtained when the formation of acid oxalate is just complete. The change in the direction varies with the dilution and becomes less distinct with increasing concentration. The sodium hydroxide employed must be free from carbonate, otherwise high results are obtained. By the use of $N/2$ sodium hydroxide solution, quantities not exceeding 0·8 g. may be satisfactorily titrated. Edgar[8] considers

[1] *Z. anal. Chem.*, 1889, **28**, 1.

[2] *Z. Verein Rubenzuckerind.*, **39**, 638.

[3] *J. Phys. Chem.*, 1910, **8**, 12; also Dutoit and Mojoin, *ibid.*, 1910, **8**, 27; and Dutoit and Von Weisse, *ibid.*, 1911, **9**, 579.

[4] *J. Amer. Chem. Soc.*, 1914, **36**, 1793.

[5] *Trans. Amer. Electrochem. Soc.*, 1914, **26**, 91.

[6] *J. Amer. Chem. Soc.*, 1913, **35**, 1527.

[7] *J. Amer. Chem. Soc.*, 1918, **40**, 1213. *Cf.* also *ibid.*, 1917, **39**, 252.

[8] *J. Amer. Chem. Soc.*, 1917, **39**, 914.

that the end point of oxidation or of reduction reactions may be determined by measurement of the electrical conductivity with a degree of accuracy equal to or exceeding that of the usual volumetric method. Further work has been carried out by I. M. Kolthoff[1] and others.

The Dionic Water Tester[2] is a device whereby the amount of dissolved substance in water or other solvent can be readily determined, when the nature of the dissolved substance is known, by a measurement of the electrical conductivity of the solution. It has already been pointed out that owing to the existence of polarisation effects at the electrodes when direct current is passed through an

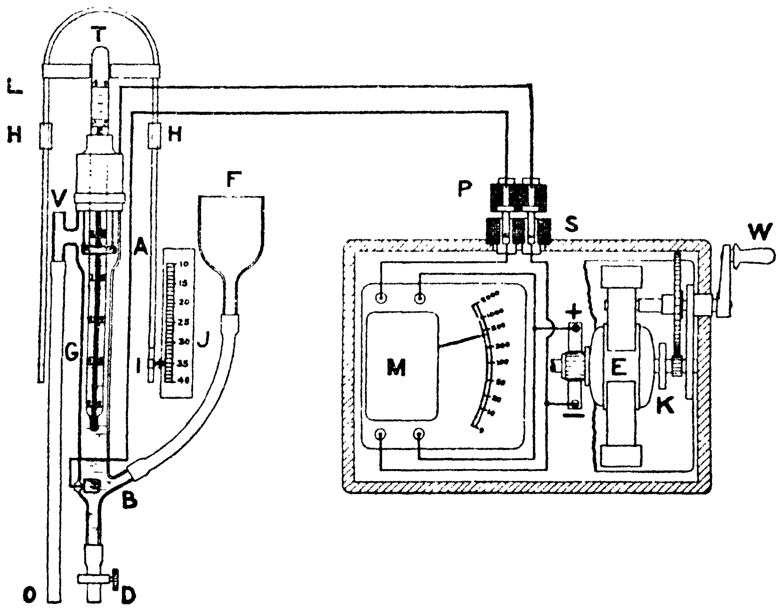


FIG. 123.

electrolyte, measurements of electrolytic conductivity are liable to considerable error unless special precautions are taken, such as the use of secondary electrodes. The Dionic Water Tester employs direct current, and is illustrated in Fig. 123. The effect of polarisation is taken into account in calibrating the scale of the instrument. G is a glass tube to contain the water under test, and A and B are the electrodes. These electrodes are connected to a continuous current hand-driven dynamo E, and to a direct conductivity meter M. The thermometer T measures the temperature of the water under test, and can be lowered or raised in the water, so altering the effective cross-sectional area of the electrolyte. It is supported in a sliding holder L

[1] *Z. anorg. Chem.*, 1920, III, I, 28, 97, 155 165, 187, etc.
[2] Supplied by Messrs Evershed & Vignoles, Ltd., Chiswick.

moving in guides H H, and which carries an index I ranging over a scale J calibrated in degrees centigrade. After the water to be tested has been passed into the funnel F and fills the tube G, the reading on the thermometer is noted; and its sliding holder is moved until the reading of the index I on the scale J corresponds with the thermometer reading. This operation compensates for the change of conductivity due to temperature. By turning the handle W of the dynamo clockwise, a current is generated which traverses the meter and the water in G. The pointer of the meter is deflected and comes to rest at a point which indicates directly the conductivity of the water at 20°. The unit of conductivity chosen is the megohm^{-1} cm.$^{-1}$, and the scale extends up to 2000 units. The handle W is turned at any speed above that at which the clutch is felt to slip (about 100 revolutions per minute). The range of temperature for which compensation is afforded is from 10° to 40°, so that the water must be warmed if below 10°, and must be cooled if above 40°. Where the conductivity of the water to be tested is higher than the maximum scale reading, the water is suitably diluted so as to bring its conductivity within the range of the instrument. A special type of conductivity tube is supplied for the measurement of high conductivity liquids such as sea-water and pathological liquids.

The Kelly Electrometric Titration apparatus[1] enables rapid determinations of the conductivity of electrolytes to be made, and is more especially designed for the determination of chromium, vanadium, and manganese in steel and ferrous alloys by the measurement of the change of oxidation potential. Chromium can be determined correctly to 0·1 per cent. when the chromium content is as high as 20 per cent.; when the chromium content is from 0·20 per cent. to 3 per cent., an accuracy of 0·01 per cent. is easily obtainable. With a chromium content of less than 0·20 per cent., it is possible to obtain an accuracy of 0·002 to 0·003 per cent. The end points are sharp and easily determined.

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[1] Made by the Leeds and Northrup Company. Sold by the A. H. Thomas Company, Philadelphia, U.S.A.

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TECHNICAL GAS ANALYSIS

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Introduction.—The analysis of gases is undertaken chiefly as a method of examination of gaseous fuels and of products of combustion. It is also a most important method of analysis in the alkali industry, in the production of illuminating gas, and in many other branches of chemical manufacture.

This section is restricted to a description of the general methods employed in technical gas analysis, and of typical forms of apparatus that are in general use. The more special methods that are employed only in special industries, either as methods of control or for the testing of final products, are described in the respective sections.

The scientific foundations of the methods of volumetric gas analysis were laid by Bunsen, who embodied his chemical researches on the subject in his work on gasometry,[2] published in 1857. The methods adopted by him have since been considerably amplified by numerous other workers, and have at the same time been rendered more available for technical work by the construction of apparatus specially suitable for this purpose, in which greater rapidity is obtained without material sacrifice of accuracy.

The method of gas analysis depends upon the successive conversion of single constituents of a gaseous mixture into a non-gaseous state either by treatment with suitable absorbing reagents and measuring the resulting diminution in volume; or by oxidation to compounds, the volume of which can be ascertained either from the contraction in volume that has occurred, or from the volume of an absorbable gas that has been formed. There are a few gases, of which nitrogen is the most

[1] The authors are indebted to Dr H. G. Colman for permission to include in this Section a portion of the subject-matter which was included in the Section on "Illuminating Gas and Ammonia" in the previous edition.

[2] *Gasometrische Methoden*, 2nd edition, 1887; English translation of 1st edition by Sir H. E. Roscoe, *Gasometry*, 1857.

important in technical work, for which no suitable absorbent or method of oxidation is known, and which are accordingly left as a residue after the estimation of other constituents.

Within recent years many forms of automatic apparatus have been devised for the rapid and continuous estimation of carbon dioxide in furnace gases. These have proved of great value for the control of combustion processes, and some of them are applicable to other purposes. They now form an important adjunct to the ordinary methods of gas analysis.

The term *gas-volumetric analysis* is applied, in a restricted sense, to methods of analysis in which a solid or a liquid substance is estimated by the generation and measurement of a gas. As they are to some extent general in character and somewhat apart from the ordinary methods of gas analysis, the apparatus employed and their applications have been included in the general introductory section (pp. 74 to 89).

The general methods of gas analysis are not applicable when the constituents concerned are present in too small quantities to be estimated by a diminution in volume, as in the case of carbon disulphide and naphthalene in illuminating gas, and of impurities in atmospheric air. For such estimations special gravimetic, volumetric, or colorimetric methods are employed, which allow of the treatment of much larger volumes of gas than is practicable by the ordinary methods of gas analysis.

Sampling.—In all branches of gas analysis the proper taking of the sample is quite as important as the method of analysis adopted. In the case of chimney gases, samples may be regarded as having a fairly constant composition if the charging is done by means of a hopper, or by some continuous mechanical process, but with ordinary intermittent charging the composition varies considerably: this is illustrated in the following data obtained in the firing of a boiler furnace:—

	1 Minute after Stoking.	12 Minutes later.
Carbon dioxide . .	13·5 per cent.	4·0 per cent.
Carbon monoxide . .	0 ,,	0 ,,
Oxygen . . .	5·5 ,,	16·5 ,,
Nitrogen . . .	81·0 ,,	79·5 ,,
Soot	Present	0 ,,

In such an instance the analysis of a single sample is seldom of value. So-called *average samples* are also unsatisfactory, because even when a constant method of suction is used for taking the sample, it is hardly possible to collect such a fraction for analysis as really represents the composition of the whole.

A reliable criterion of the course of a combustion can only be

obtained by the analysis of a series of separate samples taken at successive short intervals; the effect of the stoking and similar influences can then be gauged. If the nature of the fuel is fairly well known, the possible presence of appreciable quantities of carbon monoxide and of other combustible gases can be judged from the total of carbon dioxide and oxygen present, and the determination of the two latter gases suffices.[1]

In order to determine the small quantities of combustible gases which may occasionally be present in normal chimney gases, even accurate volumetric methods are insufficient, and gravimetric methods of analysis must be employed; these are carried out by drawing the sample for a sufficient length of time through a suitable absorption apparatus, whilst at the same time a gas-volumetric test is made every five or ten minutes, in order to follow the course of the combustion.[2]

In non-intermittent processes, other than the combustion of fuel, a suitably collected average sample may be regarded as satisfactory.

The sampling is effected by drawing the gases from the flue or chimney, through connecting tubes, into a suitable containing vessel. The sampling tube is inserted in such a position in the flue, etc., from which the sample is to be taken, that its open end is exposed to the main current of ascending gas; in the case of large chimneys or mains, a tube having a longitudinal slit or a series of fine holes is advantageous for securing a sample of average composition. The interposition of a T-tube attachment, provided with an independent aspirator, between the main sampling tube and the collecting tube, so as to "tap" the supply, is a convenient means of obtaining a representative sample of a large volume of gas.

Before collecting the sample, the air originally contained in the

[1] Since $C + O_2 = CO_2$, the 21 per cent. of oxygen in air gives 21 per cent. of carbon dioxide; for the combustion of hydrogen every 2 kilos use up 11·15 cb.m. of oxygen. In a coal having the composition :—

Carbon	. . . . .	84 per cent.
Hydrogen	. . . . .	4 ,,
Oxygen	. . . . .	8 ,,
Ash, water, etc.	. . . .	4 ,,

the burning of 1 kilo involves the consumption of air required for 0·84 kilo carbon and 0·03 kilo hydrogen, the contained oxygen of the fuel sufficing for the combustion of the rest of the hydrogen. For every $\frac{84}{12} = 7 \times 22{\cdot}3 = 156{\cdot}1$ cb.m. of carbon dioxide formed, $\frac{3}{4} \times 11{\cdot}15 = 0{\cdot}75 \times 22{\cdot}3 = 16{\cdot}75$ cb.m. of oxygen disappear from the gaseous products, owing to the combustion of the hydrogen. If, therefore, the chimney gases contain 14 per cent. of carbon dioxide, the average free oxygen, when combustion is complete, will be $21 - \left(14 - \frac{16{\cdot}75 \times 14}{156{\cdot}1}\right) = 5{\cdot}5$ per cent. After a fresh stoking the proportion of free oxygen decreases to 4-5 per cent., but increases to 6-7 per cent. when the charge is spent. The analytical results should be in accord with these data, and should always be carefully checked if this is not the case.

[2] Cf. *Dingl. polyt. J.*, 1884, **251**, 323; *Fischer's Jahresber.*, 1885, **31**, 1295.

sampling tube, the connecting tubes, and any other intermediate apparatus, must be completely displaced; to ensure this removal, at least from four to five times the capacity of the apparatus concerned should be replaced by the gas before drawing the sample for analysis.

To prevent soot, dust, or ashes entering the collecting vessel, a portion of the sampling tube is fitted with a filter of asbestos or glass wool.

The material of the connecting tube must resist the prevailing temperature, and must be unaffected by the constituents of the gas. Glass tubes are used whenever possible; they can be safely employed for temperatures up to 500° or 600°. Above this, quartz or porcelain tubes are used. Quartz tubes can be employed only up to 1000° as they become porous above this temperature; porcelain tubes necessitate gradual heating up, owing to their liability to crack. Iron and other metal tubes should be avoided; in presence of oxygen, iron tubes effect a considerable absorption of this gas, even at low temperatures, and give it off to reducing gases.

When quartz or porcelain tubes are used for aspirating hot gases, the tubes should be long enough to secure the cooling down of the sample before it enters the collecting vessel. This is sometimes effected by surrounding the tube with a water-condenser made of copper or iron. The sampling tubes are held in position by a perforated cork or rubber stopper when the temperature permits, or else by fireclay or cement.

Apparatus for Aspirating and Collecting Samples of Gases.—If the gas to be sampled is under pressure, the collecting vessel is easily filled; otherwise an aspirator must be employed. Various forms of glass aspirators, water-pumps, and small india-rubber aspirators are used. They are attached to the collecting vessel, which is connected directly with the sampling tube. More generally a form of apparatus is employed which serves both as an aspirator and for the collecting of the sample, such as the gas sampler devised by Stead[1] (Fig. 124), by means of which the sample can be aspirated and subsequently readily transferred for analysis. The gas-collector H is provided with four stopcocks, of which C is attached to the reservoir A by means of a stout piece of rubber tubing. The reservoir is filled with mercury or water, according to the nature of the sample to be taken. By placing the reservoir on the shelf B,

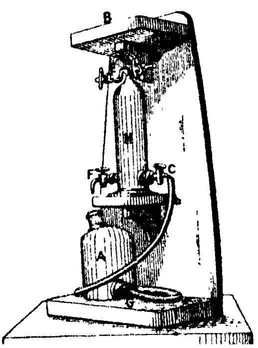

FIG. 124.

[1] *J. Soc. Chem. Ind.*, 1889, 8, 176.

and opening the taps C and D, the air in H is expelled and replaced by the mercury. The taps C and D are then closed, the connecting tube from the flue or chimney connected to E, and the reservoir lowered; by now opening D and E, the gas is drawn through the collecting tube and the upper tubes of the aspirator, thereby completely removing the contained air. D is then closed, the reservoir placed under the tap F, and the latter opened, when the mercury flows out, thereby drawing in the gas, the rate of entrance of the gas being regulated by the rate of flow of the mercury. After the sample has been collected, the taps are closed and the gas transferred for analysis, by placing the reservoir on B and opening the stopcocks C and D, sufficient gas being first allowed to escape to clear the con-

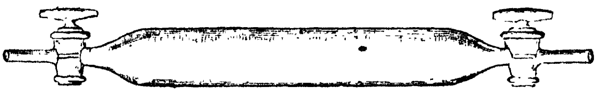

FIG. 125.

necting tubes. If the sample is to be kept for some time, it is well to put the gas under slight pressure, by opening C, whilst the reservoir is on the shelf, after the sample has been collected. A similar form of sampler has been described by Kent Smith and Towers.[1]

When the gas sample is submitted at once to analysis, the burette and pressure tube used for the analysis of the gas can be directly employed as the collecting vessel and aspirator. This is often done, especially in the control of processes and with the less exact forms of gas analysis apparatus such as that of Orsat (p. 272 *et seq.*). The removal of all intervening air must be very carefully ascertained if this method of collection is adopted.

If a number of samples are required for transport, light glass cylinders of about 100 c.c. capacity, provided with well-ground stopcocks at either end, may be used (Fig. 125). If the cylinders are provided with three-way stopcocks, the transference of the gas sample for analysis is greatly facilitated.

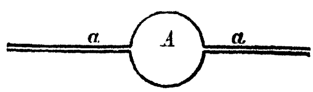

FIG. 126.

If the samples have to be kept for a considerable time before analysis, it is preferable to seal the collecting vessel hermetically. For this purpose, glass bulbs of about 100 c.c. capacity (Fig. 126) are used, which are attached to the sampling tube as described later (see Fig. 130). After being filled, they are sealed off at *a*, on either side. Should it be necessary to seal off the tubes in the open, a small oil lamp (Figs. 127 and 128, half actual size) may be advantageously used. It is provided with a wickholder *d*, and a metal cover B, having air-holes at the bottom *c*, a

[1] *J. Soc. Chem. Ind.*, 1897, 16, 400.

larger opening at the top, and a round hole *e* at the side, through which the blowpipe flame, blown from the blowpipe *n* (to which a rubber tube and mouthpiece are attached) is directed.

A very efficient and simple gas sampling tube (Fig. 129) has been devised by G. N. Huntly,[1] in which use is made of the well-known principle of the Marriotte bottle. The gas is drawn in at A. The dead space is cleared by sucking at B. The rate at which gas is drawn in is fixed by the tap and the distance CD, and the latter can be increased by joining on a glass tube with rubber to the exit tap. It is obvious that the gas cannot be sucked back or diffuse back. It has been found by trial that the rate at which the gas is drawn in is constant throughout within 1 per cent. A slight inclination of the tube from the vertical gives a sensitive fine adjustment.

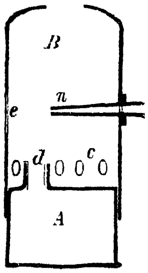

FIG. 127.

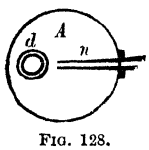

FIG. 128.

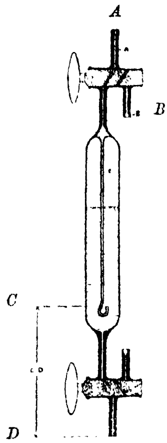

FIG. 129.

An automatic gas-sampling tube which permits a continuous sample of gas to be taken at a uniform rate has been described by T. Gray.[2] The sample is drawn by a filter pump and tapped into a collecting vessel, the filling of which is controlled by a counterpoise.

To collect the gases from a Bessemer converter, F. Fischer uses a porcelain tube (Fig. 130), placed inside an iron tube *b*, the two being held together at *a* by a collar of fireclay, and the porcelain tube projecting about 5 cm. beyond the iron tube. The porcelain tube is connected with the glass tube *z* at *c*, by a joint made with a mixture of clay and water glass; the glass tube is connected by rubber tubing *g* to a series of bulbs *n*, the last of which is attached to a small rubber aspirator. To collect the sample, the tube is placed in an upright position over the mouth of the converter, so that it is in the centre of the current of gas; the sample is then aspirated through the bulbs, one of which is sealed off and removed every two minutes.

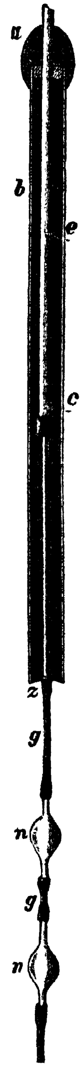

FIG. 130.

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 312. The tube is made by C. L. Müller, 6 Orange Street, London, W.C.

[2] *J. Soc. Chem. Ind.*, 1913, **32**, 1092.

Lubrication of Stopcocks employed in Gas Analysis.—The efficient lubrication of stopcocks used in gas analysis apparatus requires considerable attention. Good lubrication is, in general, afforded by a film of lubricant approaching molecular dimensions in thickness, and no improvement is produced by the indiscriminate covering of the plug with lubricant. The following lubricant is recommended by Sir Herbert Jackson. Six parts of black rubber are heated with five parts of vaseline and one part of solid paraffin until the whole of the rubber dissolves, at a temperature which causes considerable evolution of vapour from the vaseline, but without burning the rubber. The lubricant is allowed to cool, and is applied to the plug in small quantity, the plug and barrel having been previously cleaned by a soft duster, taking care that no grit remains on either plug or barrel. It is necessary to avoid closing with lubricant the hole drilled through the plug. The plug is inserted in the barrel and turned several times, until the tap appears quite transparent and streaks are entirely absent. Especial care should be taken in the lubrication of the taps of explosion vessels. On no account must any lubricant be present in the tubes leading to the stopcock, for it would be burnt when the gaseous mixture in the vessel is exploded, and the analytical result be very much in error on this account. The minimum of the lubricant described above is therefore very carefully applied to the plug, or, preferably, phosphoric acid should be used to lubricate such stopcocks.

Clips for connecting Gas-Analysis Apparatus.—A useful clip for preventing rubber connections from slipping off glass and metal tubing has been designed by C. A. Keane and G. Patchin.[1] It is adaptable to many forms of apparatus, and is particularly useful in that employed for gas analysis.

The clip is easily and quickly adjusted, it does not wear or cut the rubber tubing, and it possesses sufficient play to be adaptable to any slight variations in the size of the connections concerned. It is quite reliable for securing the connections in apparatus in which mercury is employed as the confining liquid.

The general design of the clip is shown open and closed and in use with a Hempel gas burette and pipette in Fig. 131 (p. 236).

Correction of Volume of Gas for Temperature and Pressure.—It is customary to distinguish between "exact" and "technical" gas analysis according to the method of working adopted. In the former, mercury is usually employed as the confining liquid, and the smallest possible quantities of liquid are used for the absorption of the gases, so as to avoid the simultaneous absorption of other gases which are

[1] *J. Soc. Chem. Ind.*, 1917, **38**, 391T. The clip is made by Messrs Baird & Tatlock, Cross Street, London, E.C. 1, as the "K-P" clip, in several sizes.

dissolved to a slight extent by aqueous solutions; also, the pressure and temperature are taken for each reading, and the gas volume corrected to normal conditions. The normal temperature most generally employed is 0° C., and the pressure that due to a column of mercury 760 mm. in height and of density 13·596. If the percentage composition of a gaseous mixture is to be expressed to the second place of decimals—indeed, if the principal exponents of the mixture are to be expressed to one significant decimal place—the barometric height ought, throughout the analysis, to be reduced to the standard

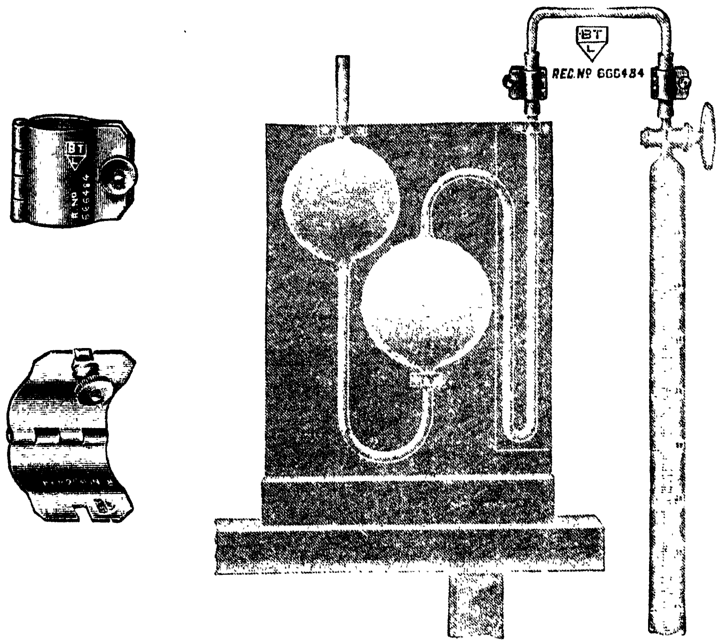

FIG. 131.

temperature of 0° C. Such a correction is sometimes applied in technical gas analysis—more especially in the analysis of coal-gas—but for most purposes of technical gas analysis the correction is omitted. Frequently, more especially in technical gas works analysis, the standard conditions of temperature and pressure are specified as 60° F. and a pressure of 30 ins. of mercury, the gas being saturated with water vapour. A series of so-called "tabular numbers" enabling measured volumes of moist gas to be reduced to these standard conditions readily is contained in the table on pp. 238-9, the figures given representing the volumes of gas which, if reduced to standard conditions, would have unit volume. The corresponding correction is

therefore effected by *dividing* by the appropriate tabular number. In general, if

V = volume as read at $t°$ C.
V_0 = volume corrected to 0° C. and 760 mm. of mercury pressure.
B = barometric height in mm. of mercury at time of experiment.
h = deficit of pressure from atmospheric in burette at time of experiment.
T = vapour pressure of water at $t°$ expressed in mm. of mercury.

Then $V_0 = \dfrac{V \times (B - T)}{(1 + 0.003665t)\,760}$ if the gas is saturated with water vapour,

and $V_0 = \dfrac{VB}{(1 + 0.003665t)\,760}$ if the gas is dry.

It may here be mentioned that unless a correction is made, a variation of 7 mm. in pressure or of 3° C. in temperature, introduces an error of about 1 per cent. in the percentage analysis of the gas. The most effective means of minimising changes in temperature is to provide the measuring tube of the apparatus with a water-jacket, and if possible to run a current of water of constant temperature through the jacket during the test. In the more accurate forms of apparatus in which mercury is used as the confining liquid, a compensating or "correction" tube is attached to the measuring tube by means of which the gas-volumes are automatically corrected to normal temperature and pressure (see p. 290).

Solubility of Gases in Water.

Gas.	Solubility in Water.		
	At 0°	At 15°	At 30°
Acetylene	A 1·730	1·208	0·934
Ammonia	A 1299	802	595/28°
Argon	A 0·058	0·040	0·030
Carbon dioxide	A 1·713	1·019	0·665
Carbon monoxide	A 0·0354	0·0254	0·020
Chlorine	...	S 2·635	1·769
Cyanogen	...	α 4·05	...
Ethane	A 0·098	0·058	0·040
Ethylene	A 0·226	0·109	...
Helium	A 0·0150	0·0139	0·0138
Hydriodic acid	...	A 425/10°	...
Hydrobromic acid	S 612	565	517
Hydrochloric acid	S 506·7	458·4	411·5
Hydrogen	A 0·0215	0·0190	0·0170
Hydrogen sulphide	A 4·686	3·056	2·24
Methane	A 0·0556	0·0369	0·0276
Nitric oxide	A 0·074	0·051	0·040
Nitrogen	A 0·0239	0·0179	0·0138
Nitrous oxide	A 1·05/5°	0·74	0·63/20°
Oxygen	A 0·0489	0·0342	0·0261
Ozone	α 0·64	0·46	0·19/32°
Propane	...	A 0·065/18°	...
Propylene	α 0·446	0·279	...
Sulphur dioxide	S 79·8	47·8	27·2
Air	A 0·0294	0·0205	0·0157

Tabular Numbers, being a Table to facilitate the Correction represented by 60° F. and

GAS VOLUMES.—*The numbers in this table are the volumes of gas saturated from the formula* $V = \dfrac{459{\cdot}4 + t}{17.617(h\text{-}a)}$, *where* V *is the volume, vapour pressure of water at* $t°$, *and* t *the*

Barometer—Inches of Mercury.	Temperature—Fahrenheit.														
	40°	42°	44°	46°	48°	50°	52°	54°	56°	57°	58°	59°	60°	61°	62°
28·0	1·022	1·026	1·031	1·036	1·041	1·046	1·051	1·057	1·062	1·065	1·067	1·070	1·073	1·076	1·078
28·1	1·018	1·023	1·027	1·032	1·037	1·042	1·048	1·053	1·058	1·061	1·063	1·066	1·069	1·072	1·075
28·2	1·014	1·019	1·024	1·029	1·034	1·039	1·044	1·049	1·054	1·057	1·060	1·062	1·065	1·068	1·071
28·3	1·011	1·015	1·020	1·025	1·030	1·035	1·040	1·045	1·050	1·053	1·056	1·059	1·061	1·064	1·067
28·4	1·007	1·012	1·017	1·021	1·026	1·031	1·036	1·042	1·047	1·049	1·052	1·055	1·057	1·060	1·063
28·5	1·003	1·008	1·013	1·018	1·023	1·028	1·033	1·038	1·043	1·046	1·048	1·051	1·054	1·056	1·059
28·6	1·000	1·005	1·009	1·014	1·019	1·024	1·029	1·034	1·039	1·042	1·045	1·047	1·050	1·053	1·055
28·7	·996	1·001	1·006	1·011	1·015	1·020	1·025	1·030	1·036	1·038	1·041	1·044	1·046	1·049	1·052
28·8	·993	·997	1·002	1·007	1·012	1·017	1·022	1·027	1·032	1·035	1·037	1·040	1·043	1·045	1·048
28·9	·989	·994	·999	1·004	1·008	1·013	1·018	1·023	1·028	1·031	1·034	1·036	1·039	1·042	1·044
29·0	·986	·991	·995	1·000	1·005	1·010	1·015	1·020	1·025	1·027	1·030	1·033	1·035	1·038	1·041
29·1	·983	·987	·992	·997	1·001	1·006	1·011	1·016	1·021	1·024	1·026	1·029	1·032	1·034	1·037
29·2	·979	·984	·988	·993	·998	1·003	1·008	1·013	1·018	1·020	1·023	1·026	1·028	1·031	1·033
29·3	·976	·980	·985	·990	·994	·999	1·004	1·009	1·014	1·017	1·019	1·022	1·024	1·027	1·030
29·4	·972	·977	·982	·986	·991	·996	1·001	1·006	1·011	1·013	1·016	1·018	1·021	1·023	1·026
29·5	·969	·974	·978	·933	·988	·992	·997	1·002	1·007	1·010	1·012	1·015	1·017	1·020	1·023
29·6	·966	·970	·975	·980	·984	·989	·994	·999	1·004	1·006	1·009	1·011	1·014	1·016	1·019
29·7	·963	·967	·972	·976	·981	·986	·990	·995	1·000	1·003	1·005	1·008	1·010	1·013	1·016
29·8	·959	·964	·968	·973	·978	·982	·987	·992	·997	·999	1·002	1·004	1·007	1·009	1·012
29·9	·956	·960	·965	·970	·974	·979	·984	·938	·993	·996	·998	1·001	1·003	1·006	1·009
30·0	·953	·957	·962	·966	·971	·976	·980	·985	·990	·992	·995	·998	1·000	1·003	1·005
30·1	·950	·954	·959	·963	·968	·972	·977	·982	·987	·989	·992	·994	·997	·999	1·002
30·2	·946	·951	·955	·960	·964	·969	·974	·979	·983	·986	·988	·991	·993	·996	·998
30·3	·943	·948	·952	·957	·961	·966	·970	·975	·980	·982	·985	·987	·990	·992	·995
30·4	·940	·945	·949	·953	·958	·963	·967	·972	·977	·979	·982	·984	·987	·989	·992
30·5	·937	·941	·946	·950	·955	·959	·964	·969	·974	·976	·978	·981	·983	·986	·988
30·6	·934	·938	·943	·947	·952	·956	·961	·966	·970	·973	·975	·978	·980	·983	·985
30·7	·931	·935	·940	·944	·949	·953	·958	·962	·967	·970	·972	·974	·977	·979	·982
30·8	·928	·932	·937	·941	·945	·950	·955	·959	·964	·966	·969	·971	·974	·976	·979
30·9	·925	·929	·933	·938	·942	·947	·951	·956	·961	·963	·966	·968	·970	·973	·975
31·0	·922	·926	·930	·935	·939	·944	·948	·953	·958	·960	·962	·965	·967	·970	·972

[1] From the notification of Gas Referees, 1918, by

of Gaseous Volumes measured Moist to Standard Conditions 30 inches of mercury pressure.[1]

with water vapour at different temperatures and pressures. They are calculated

h the pressure of the gas in inches of mercury, a the

temperature on the Fahrenheit scale.

Barometer—Inches of Mercury.	Temperature—Fahrenheit.														
	63°	64°	65°	66°	67°	68°	69°	70°	72°	74°	76°	78°	80°	82°	84°
28·0	1·081	1·084	1·087	1·090	1·093	1·096	1·099	1·102	1·108	1·115	1·121	1·128	1·135	1·142	1·149
28·1	1·077	1·080	1·083	1·086	1·089	1·092	1·095	1·098	1·104	1·111	1·117	1·124	1·131	1·138	1·145
28·2	1·074	1·076	1·079	1·082	1·085	1·088	1·091	1·094	1·100	1·107	1·113	1·120	1·127	1·134	1·141
28·3	1·070	1·072	1·075	1·078	1·081	1·084	1·087	1·090	1·096	1·103	1·109	1·116	1·123	1·130	1·137
28·4	1·066	1·069	1·071	1·074	1·077	1·080	1·083	1·086	1·092	1·099	1·105	1·112	1·118	1·125	1·133
28·5	1·062	1·065	1·068	1·070	1·073	1·076	1·079	1·082	1·088	1·095	1·101	1·108	1·114	1·121	1·128
28·6	1·058	1·061	1·064	1·067	1·070	1·072	1·075	1·078	1·084	1·091	1·097	1·104	1·110	1·117	1·124
28·7	1·054	1·057	1·060	1·063	1·066	1·069	1·072	1·075	1·081	1·087	1·093	1·100	1·106	1·113	1·120
28·8	1·051	1·053	1·056	1·059	1·062	1·065	1·068	1·071	1·077	1·083	1·089	1·096	1·102	1·109	1·116
28·9	1·047	1·050	1·053	1·055	1·058	1·061	1·064	1·067	1·073	1·079	1·085	1·092	1·098	1·105	1·112
29·0	1·043	1·046	1·049	1·052	1·054	1·057	1·060	1·063	1·069	1·075	1·081	1·088	1·094	1·101	1·108
29·1	1·040	1·042	1·045	1·048	1·051	1·054	1·056	1·059	1·065	1·071	1·078	1·084	1·091	1·097	1·104
29·2	1·036	1·039	1·041	1·044	1·047	1·050	1·053	1·056	1·062	1·068	1·074	1·080	1·087	1·093	1·100
29·3	1·032	1·035	1·038	1·041	1·043	1·046	1·049	1·052	1·058	1·064	1·070	1·076	1·083	1·090	1·096
29·4	1·029	1·032	1·034	1·037	1·040	1·043	1·045	1·048	1·054	1·060	1·066	1·073	1·079	1·086	1·092
29·5	1·025	1·028	1·031	1·033	1·036	1·039	1·042	1·045	1·050	1·056	1·063	1·069	1·075	1·082	1·089
29·6	1·022	1·024	1·027	1·030	1·033	1·035	1·038	1·041	1·047	1·053	1·059	1·065	1·071	1·078	1·085
29·7	1·018	1·021	1·024	1·026	1·029	1·032	1·035	1·037	1·043	1·049	1·055	1·061	1·068	1·074	1·081
29·8	1·015	1·017	1·020	1·023	1·025	1·028	1·031	1·034	1·040	1·046	1·052	1·058	1·064	1·071	1·077
29·9	1·011	1·014	1·017	1·019	1·022	1·025	1·028	1·030	1·036	1·042	1·048	1·054	1·060	1·067	1·073
30·0	1·008	1·010	1·013	1·016	1·019	1·021	1·024	1·027	1·033	1·038	1·044	1·050	1·057	1·063	1·070
30·1	1·004	1·007	1·010	1·012	1·015	1·018	1·021	1·023	1·029	1·035	1·041	1·047	1·053	1·059	1·066
30·2	1·001	1·004	1·006	1·009	1·012	1·014	1·017	1·020	1·025	1·031	1·037	1·043	1·049	1·056	1·062
30·3	·998	1·000	1·003	1·006	1·008	1·011	1·014	1·016	1·022	1·028	1·034	1·040	1·046	1·052	1·059
30·4	·994	·997	1·000	1·002	1·005	1·007	1·010	1·013	1·019	1·024	1·030	1·036	1·042	1·049	1·055
30·5	·991	·994	·996	·999	1·001	1·004	1·007	1·010	1·015	1·021	1·027	1·033	1·039	1·045	1·052
30·6	·988	·990	·993	·995	·998	1·001	1·003	1·006	1·012	1·017	1·023	1·029	1·035	1·042	1·048
30·7	·984	·987	·990	·992	·995	·997	1·000	1·003	1·008	1·014	1·020	1·026	1·032	1·038	1·044
30·8	·981	·984	·986	·989	·991	·994	·997	1·000	1·005	1·011	1·016	1·022	1·028	1·035	1·041
30·9	·978	·980	·983	·986	·988	·991	·993	·996	1·002	1·007	1·013	1·019	1·025	1·031	1·037
31·0	·975	·977	·980	·982	·985	·988	·990	·993	·998	1·004	1·010	1·015	1·021	1·028	1·034

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In technical gas analysis, water, and occasionally aqueous solutions, are used as the confining liquid, and no correction is made for the solubility of the gases. The table on p. 237 gives particulars of the solubilities of various gases in water, so far as these have been determined at the temperatures specified.

The symbols A, S, and α in the table on p. 237 are used with the following significance. Winkler draws a distinction between the terms coefficients of absorption and solubility. The solubility is indicated by S in the table, and is that volume of the gas (reduced to 0° C. and 760 mm.) which is dissolved by unit volume of the solvent (water) when the total pressure at the surface of the liquid (*i.e.*, pressure of gas + vapour pressure of water) is 760 mm. The coefficient of absorption, A, he defines as the volume of the gas (reduced to 0° C. and 760 mm.) dissolved by unit volume of the solvent (water) when the pressure of the gas alone is 760 mm. Winkler also points out that the vapour pressure of the solvent in contact with the solution may differ from its value when the solvent evaporates into an otherwise vacuous space, on account of the presence of the gas in the liquid, or for other reasons. α denotes the coefficient of absorption as the term was used by Bunsen, and is the volume occupied at 0° C. and 760 mm. by the gas contained in unit volume *of the solution*. The respective symbols S, A, and α in the table apply to all the solubility data given for the respective gases for all the specified temperatures.

The error introduced by solubility is sometimes compensated by previously saturating both the confining liquid and the absorption reagents with the gas to be analysed, or with gas of similar composition.

GENERAL METHODS OF GAS ANALYSIS

The various methods employed in technical gas analysis may be classified as follows:—

1. **Method of Direct Absorption.**—Some gases are determined by direct absorption by certain reagents, the diminution of the volume indicating the quantity of the gas in question present.
2. **Method of Indirect Determination.**—Combustible gases are frequently determined by explosion, or by combustion at a high temperature, with excess of air or oxygen. The components are determined from the diminution in volume after explosion or combustion, the quantity of carbon dioxide formed, and the quantity of oxygen consumed as determined by absorption of the residual oxygen.

   Oxygen may be determined by explosion with excess of hydrogen when other combustible gases are absent.

Fractional Combustion.—Certain gases can be determined by fractional combustion, using an oxidising agent either with or without a catalyst at a carefully controlled temperature.

3. **Special Methods of Determination.**—The above methods are not generally applicable when it is desired to determine gases present to the extent of 0·2 per cent. or less in gaseous mixtures, and special methods giving a high degree of accuracy are then employed.

1. Direct Determination by Absorption

Bunsen absorbed the constituents of a gaseous mixture by means of various solid reagents shaped into bullets and attached to a platinum wire. Occasionally the absorbent was employed in the form of a solid medium impregnated with a liquid absorbent. These solid reagents are now very seldom used. In all modern apparatus, gases which are to be determined by direct absorption are brought into intimate contact with the appropriate liquid or dissolved absorbent in an absorption vessel, separate from but having connection with the measuring vessel. The following are the absorbents principally employed for the absorption of the gases specified, which are arranged in alphabetical order.

Acetylene is absorbed in an ammoniacal solution of silver chloride prepared by saturating pure concentrated ammonia solution (sp. gr. 0·880) with silver chloride freshly precipitated from the nitrate. Ammonia left in the gas after the absorption, is removed by dilute sulphuric acid before any measurement is made.

Ammonia is best determined by titration, provided a sufficiently large sample of gas is available (see p. 312); but if the sample available is small, the ammonia present may be determined by absorption by a 10 per cent. solution of sulphuric acid. Great care must be taken that the gas is not absorbed by traces of moisture in different parts of the apparatus. It must also be remembered that the solubility of gases such as carbon dioxide in the 10 per cent. acid is considerable, and that a high result may be obtained unless the absorption is carried out quickly and with a small volume of absorbing solution.

Benzene Vapour is absorbed by concentrated sulphuric acid containing from 95 to 97 per cent. of sulphuric acid. When benzene vapour and ethylene, together with their homologues, are present in the gaseous mixture, and it is unnecessary to differentiate between these constituents, they may all be absorbed together in bromine water. Concentrated sulphuric acid also absorbs propylene and the higher olefines, but not ethylene. The use of fuming sulphuric acid

(containing about 10 per cent. free SO_3) is sometimes recommended for the absorption of benzene and the olefines.

If the absorption be effected by concentrated or fuming sulphuric acid, shaking must be continued for three to five minutes to effect complete absorption, and before re-measuring, the gas must be passed over potassium hydroxide solution to remove the vapours of sulphur dioxide, etc. Where a large bulk of fuming acid is employed, as in the Hempel apparatus, oxygen, if present, is absorbed to a small extent, probably by the compounds formed from the hydrocarbons and sulphuric acid; it should therefore be removed previously.

The absorption with bromine is carried out with a solution of bromine in water or in potassium bromide solution. The olefines are very rapidly converted into dibromides, but the aromatic hydrocarbons are not chemically acted on by the bromine, their removal being simply mechanical; a period of three minutes should be allowed for their absorption, and at the end of the time the gas should still be strongly coloured with bromine vapour. Before re-measuring, the gas must be treated with potassium hydroxide to remove the excess of bromine vapour.

The separate determination of olefines and of benzene and its homologues by special absorbents has frequently been proposed, but most of the methods have been shown to be quite unreliable. Benzene vapour may be estimated by absorption with an ammoniacal nickel nitrate solution, but only when the gas analysed also contains hydrocyanic acid, the compound formed being $C_6H_6 . NH_3 . Ni(CN)_2$. Dennis and M'Carthy[1] have recommended an ammoniacal solution of nickel cyanide, prepared as follows:—A solution of 25 g. of potassium cyanide in 25 c.c. of water is added to a solution of 50 g. of crystallised nickel sulphate in 75 c.c. of water, 125 c.c. of ammonia (sp. gr. 0·91) added, the whole cooled to 0°, and poured off from the separated potassium sulphate; 18 g. of citric acid in 10 c.c. of water is added, the solution again cooled to 0° for ten minutes, decanted from potassium sulphate crystals, and a few drops of benzene then added and shaken till combination takes place, as the solution is much more active after it has absorbed some benzene. The gas must be well shaken with the reagent for at least three minutes, and before remeasuring must be passed into dilute sulphuric acid to remove ammonia. The solution has no action on ethylene or on carbon monoxide; the former may be estimated by absorption with bromine or fuming sulphuric acid after the removal of the benzene. The small quantities of benzene homologues present are not absorbed by the reagent, but their amount rarely exceeds 0·1 per cent. Check tests given by Dennis and M'Carthy show good agreement with the theoretical figures, but a wider

[1] *J. Amer. Chem. Soc.*, 1908, **30**, 233.

experience with varied gases is necessary to establish the general applicability of the method.

In the analysis of a complex gas mixture such as coal gas, the absorption is best effected by sulphuric acid, as this absorbent can be used at an early stage in the analysis, before any of the benzene has been otherwise removed.

Special methods for the determination of benzene are described later.

Carbon Dioxide.—The absorbent mostly employed is a solution of one part of potassium hydroxide in two parts of water; contact for one minute is sufficient for complete absorption.

This reagent also absorbs hydrocarbon vapours, such as are present in coal gas, carburetted water gas, and oil gas, thus making the result for carbon dioxide from 0·1 to 0·4 per cent. too high and that for the unsaturated hydrocarbons (chiefly benzene and its homologues) too low. This effect can be avoided by using a more dilute solution (1 : 3) and not shaking the gas with the reagent.

Carbon Monoxide.—The absorbent solution used for this constituent is cuprous chloride in acid or ammoniacal solution; the latter solution is most frequently employed. Oxygen and ethylene are absorbed by the acid solution, and acetylene, in addition, by the ammoniacal solution; these constituents must therefore be removed before the estimation of the carbon monoxide.

The acid solution is prepared by dissolving 100 g. of crystallised cupric chloride in 500 c.c. of concentrated hydrochloric acid diluted with an equal volume of water, and allowing the solution to stand with an excess of metallic copper until colourless.

The acid solution cannot be used in contact with mercury, and, moreover, Drehschmidt[1] has shown that, after prolonged use, the acid solution is a less efficient absorbent than the ammoniacal solution.

For the ammoniacal solution required in the Hempel or Orsat apparatus, a very active solution is obtained by Winkler's method of preparation. A stock solution is made up by dissolving 200 g. of cuprous chloride and 250 g. of ammonium chloride in 750 c.c. of water; this solution is kept in a rubber-stoppered bottle with a few spirals of copper wire. When required for use this solution is mixed with one-third of its volume of ammonium hydroxide of sp. gr. 0·905.

For use in apparatus in which only a small volume of the reagent is employed, Bone recommends the following method of preparation. Fifty to seventy grams of white cuprous chloride are suspended in 250 c.c. of water containing 10 to 15 g. of ammonium chloride, and ammonia gas passed into the liquid (air being excluded) until no more solid dissolves and the solution smells distinctly of ammonia. A further quantity of about 5 g. of cuprous chloride is then added, the

[1] *Ber.*, 1887, **20**, 2752, and 1888, **21**, 2158.

liquid well shaken, and stored in bottles closed with a rubber stopper; after a few hours the solution should cease to smell of ammonia.

Solutions which have absorbed carbon monoxide give off some of it to indifferent gases, an equilibrium being always obtained for the carbon monoxide content between the gas and the liquid. For the complete removal of the carbon monoxide from the gas, the latter must therefore eventually be treated with a solution containing very little absorbed gas. Where small quantities of the reagent are employed, two absorptions with different portions of the fresh solution are always used; with the Hempel and similar apparatus two absorption pipettes are used in succession, the second containing solution which has absorbed only small quantities of carbon monoxide. As soon as the treatment in the second pipette shows an absorption of more than 0·4 to 0·5 per cent., the first pipette is recharged with fresh solution and used for the final absorption, the pipette previously used for this purpose being then employed for the first absorption.

Ethane and the higher paraffins can be approximately determined by absorption in absolute alcohol, using water subsequently to remove the alcohol vapour. These gases are determined most accurately, however, by explosion or by fractional combustion under certain conditions.

Ethylene.—As already mentioned, both benzene vapour and ethylene are completely removed by the action of bromine, but whereas the latter combines with bromine to form the stable compound, ethylene dibromide $C_2H_4Br_2$, benzene vapour appears to be mechanically removed as a mixture of bromine and benzene, or possibly as a very unstable additive compound, which yields up the whole of its bromine to any substance which reacts readily with bromine, such as potassium iodide. Haber and V. Oechelhäuser have based a method for estimating ethylene, and indirectly benzene, in coal gas on this difference of behaviour (see p. 297).

Taplay[1] states that if the aqueous solution of bromine is employed, the olefines may be separated from benzene, while the potassium bromide solution absorbs benzene.

If carbon monoxide is absent from the gaseous mixture, fuming nitric acid may be used to absorb benzene and olefines.

Hydrochloric Acid and the other halogen acids are best determined by titration. Bunsen used solid sodium phosphate to absorb them.

Hydrogen.—This gas is almost always determined by combustion, but occasionally Hempel's method of absorption by palladium is employed (see p. 269). Paal and Hartmann[2] have shown that hydrogen may also be determined by absorption with a solution prepared by dissolving 2·22 g. of colloidal palladium (containing 67·36

[1] *J. Gas Lighting*, 1913, **124**, 870.

[2] *Ber.*, 1910, **43**, 243.

per cent. = 1·5 g. Pd) and 2·74 g. of sodium picrate in 125 c.c. of water, the solution being placed in a Hempel or similar pipette. The absorption is somewhat slow, requiring from ten to twenty minutes, with occasional shaking. Carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide must be previously removed; as also sulphur, phosphorus, and arsenic compounds, which destroy the catalytic power of the palladium.

When the solution becomes inactive, the palladium may be recovered by carefully adding dilute sulphuric acid, drop by drop, so long as a precipitate forms, avoiding an excess. The precipitated palladium is filtered, washed, suspended in a small quantity of water, dissolved by gradual addition of sodium hydroxide solution and sodium picrate again added.[1]

K. A. Hofmann[2] recommends the use of platinum and palladium activated by a solution of sodium chlorate containing osmic acid.

Nitric Oxide may be determined by converting it to nitrogen peroxide with excess of oxygen, the peroxide being absorbed by potassium hydroxide and the excess oxygen by alkaline pyrogallate solution. Mixtures of oxides of nitrogen are best determined by titration.

Oxygen.—Either alkaline pyrogallol or phosphorus is used as the absorbent. The pyrogallol solution is made up by dissolving 20 g. of pyrogallol in 500 c.c. of potassium hydroxide solution (1 : 2), or by mixing 1 volume of aqueous pyrogallol (1 : 3) with 5 volumes of aqueous potassium hydroxide (3 : 2); this large excess of alkali is necessary, as otherwise an appreciable quantity of carbon monoxide may be formed when gases rich in oxygen are passed into pyrogallol.[3] For the analysis of oxygen prepared by Brin's process, Clowes[4] found the most suitable absorbent to be a solution of 160 g. potassium hydroxide and 10 g. pyrogallol made up to 200 c.c.; it is claimed that no evolution of carbon monoxide occurs when using this solution.

For technical work, sodium rather than potassium hydroxide is frequently preferred on account of economy. Orsat's reagent is a mixture of a concentrated solution of 25 g. pyrogallol and 150 c.c. 25 per cent. sodium hydroxide solution. Jones and Meighan[5] have investigated the efficiency of sodium pyrogallate solutions for oxygen absorption, and find that the rate of absorption increases with dilution of the sodium hydroxide, and is, moreover, proportional to the concentration of the pyrogallol for a constant concentration of the hydroxide. All sodium pyrogallate solutions evolve carbon monoxide when used

[1] Brunck, *Chem. Zeit.*, 1910, **34**, 1313, 1332.
[2] *Ber.*, 1915, **48**, 1565; 1916, **49**, 1650.
[3] *Cf.* Hempel, *Ber.*, 1885, **18**, 278; Clowes, *J. Soc. Chem. Ind.*, 1896, **15**, 170.
[4] *B. A. Report*, 1896, p. 747.
[5] *J. Ind. Eng. Chem.*, 1919, **11**, 311.

for the analysis of gas samples containing more than 95 per cent. of oxygen. For air analysis, the sodium hydroxide solution employed should have a sp. gr. not less than 1·30. A solution, which while highly efficient as an absorbent evolves a minimum of carbon monoxide, is made up as follows: The stock hydroxide solution is made by dissolving sodium hydroxide sticks in an equal weight of water; the stock pyrogallol solution contains 1 part of pyrogallol in 3 parts of water; for use, 5 parts of the hydroxide solution are mixed with 2 parts of the pyrogallol solution.

Phosphorus is a very energetic absorbent for oxygen, but its action is hindered by traces of certain gases and vapours, such as the unsaturated hydrocarbons, phosphoretted hydrogen, ammonia, and alcohol vapour; the absorption is very slow below 14°. This reagent is used in the form of thin rods, surrounded by water, in the pipette for solid absorbents, shown in Fig. 141. The phosphorous oxide fumes evolved in the absorption are removed by passing the gas into a potassium hydroxide pipette, after the absorption of oxygen is complete. The water in the pipette should be renewed from time to time, as it becomes saturated with phosphorous acid, and when not in use the pipette should be kept in the dark to avoid the formation of the inactive amorphous phosphorus. Travers[1] suggests the absorption of oxygen by phosphorous vapour when combustible gases are present. This method has been employed by Watson[2] and by Aston[3] for the determination of the oxygen content of the air.

In the case of coal gas and similar mixtures containing vapours of unsaturated hydrocarbon, H. G. Colman[4] found that the most accurate results for oxygen are obtained by using bromine for the absorption of the hydrocarbon vapours and phosphorus for the absorption of the oxygen.

Sodium hydrosulphite has also been proposed as an absorbent for oxygen;[5] it is cheaper than pyrogallol, and absorbs oxygen equally readily at various temperatures. The solution is prepared by dissolving 50 g. of the salt in 250 c.c. of water and adding 40 c.c. of a sodium hydroxide solution, containing 500 g. of alkali to 700 c.c. of water, and is used in a pipette fitted with rolls of iron gauze. The absorption takes place according to the equation:—

$$Na_2S_2O_4 + H_2O + O = 2NaHSO_3.$$

An absorbent frequently used for commercially prepared oxygen consists of copper wire kept clean and moist by means of a solution composed of equal volumes of ammonia (sp. gr. 0·930) and of a

[1] *The Experimental Study of Gases*, 1901, p. 83.

[2] *J. Chem. Soc.*, 1911, **99**, 1460.

[3] *Ibid.*, 1919, **115**, 472.

[4] Private communication.

[5] *Cf.* H. Franzen, *Ber.*, 1906, **39**, 2069.

saturated solution of commercial ammonium carbonate. Oxygen is absorbed by the exposed surface of moist copper, and the sub-oxide formed is dissolved by the ammonia solution.[1]

Propylene and the higher olefines are absorbed by concentrated sulphuric acid (see Benzene, p. 241).

Sulphur Dioxide is readily absorbed by potassium hydroxide solution, and may be thus determined, provided carbon dioxide be absent. If carbon dioxide and sulphur dioxide be both present, the latter may be titrated with iodine solution (see p. 304 *et seq.*), or it may be determined by absorption in a solution containing 450 g. of chromic acid per 1000 c.c. of water, to which 450 g. of phosphoric acid (sp. gr. 1·70) are added. The solution is brought to the boil and cooled before use.

Sulphuretted Hydrogen.—This gas is best determined by titration. If only a small sample of gas is available, the determination may be carried out by volumetric absorption in an acid solution of copper sulphate, or of cadmium sulphate or chloride. More accurate determinations, more especially of small quantities of this gas, are made as described later (see p. 304 *et seq.*).

The order in which the several absorbents are employed in the analysis of a gaseous mixture needs careful consideration. The choice of alternative absorbents will depend in part upon whether any particular constituent is being especially determined. No general rule can therefore be made as to the order in which the respective absorbents are to be used. For coal gas, which is typical of the most complex gas mixtures that may be met with in technical practice, it may be noted that Rhead and Wheeler[2] employed the following reagents in the order stated :—

Constituent.	Absorbent.
Ammonia	10 per cent. sulphuric acid.
Benzene (and higher olefines) .	Concentrated sulphuric acid.
Sulphuretted hydrogen . .	Acid solution of copper sulphate.
Carbon dioxide	33 per cent. potassium hydroxide solution.
Oxygen	Alkaline solution of potassium pyrogallate.
Acetylene	Ammoniacal solution of silver chloride.
Ethylene	Bromine-potassium bromide solution.
Carbon monoxide . . .	Ammoniacal solution of cuprous chloride.

Hydrogen was absorbed from the residue by means of oxidised palladium. Methane and ethane were determined by explosion with oxygen.

[1] See *Thorpe's Dictionary*, 1913, **4**, 44.
[2] *J. Chem. Soc.*, 1910, **97**, 1923.

2. INDIRECT DETERMINATIONS.

Many gases are determined indirectly by exploding them with another gas, and noting the alteration in volume, or the volume of the products of the explosion, or by observing both these results. Thus hydrogen may be determined by explosion with excess of air or oxygen; oxygen may be exploded with an excess of hydrogen. In each case the contraction of volume is determined on explosion. Methane may be exploded with an excess of air or oxygen, and the contraction noted together with the further diminution of volume which occurs on absorption of the carbon dioxide produced. The volume of oxygen used up in the explosion is sometimes determined by absorbing the excess.

In addition to the explosion method, the slow fractional combustion of a combustible mixture containing an excess of oxygen may be effected by means of metallic palladium.

In a third method of combustion, originally introduced by Jaeger,[1] the fractional combustion is effected in the presence of copper oxide at various temperatures (see p. 260).

The following considerations apply to all results obtained by any of these methods of combustion.

CHANGES IN VOLUME BY COMBUSTION.

The volume of combustible gases to be estimated is in a certain relation to the contraction in volume resulting from the combustion (c), to the carbon dioxide formed on combustion (CO_2), and to the sum of the hydrogen contraction plus carbon dioxide (total contraction C). The volumetric relations are shown in the table on p. 249. In the graphic representation of the volume changes, the squares enclosed by dotted lines denote the volumes which disappear by contraction, and the darkened squares the carbon dioxide formed by combustion.

Hence the volumes are as follows:—

$$
\begin{aligned}
H &= \tfrac{2}{3}c \text{ (or } \tfrac{2}{3}C) \\
CO &= CO_2, \text{ or } 2c, \text{ or } \tfrac{2}{3}C \\
CH_4 &= CO_2, \text{ or } \tfrac{1}{2}c, \text{ or } \tfrac{1}{3}C \\
C_2H_6 &= \tfrac{1}{2}CO_2, \text{ or } \tfrac{2}{5}c, \text{ or } \tfrac{2}{9}C \\
C_2H_4 &= \tfrac{1}{2}CO_2, \text{ or } \tfrac{1}{2}c, \text{ or } \tfrac{1}{4}C.
\end{aligned}
$$

If only one combustible gas be present in the mixture, in the case of carbon monoxide and of methane, their volumes may be deduced either from the contraction c, due to the carbon dioxide formed, or from the total contraction C. The latter gives the more accurate results chiefly because the volume readings are larger.

[1] *J. Gasbeleucht.*, 1898, 41, 764.

Gas.	Equation of Combustion.	Graphic Representation.	Volume of Oxygen Consumed.	The Contraction, c.	Corresponds to	Therefore	1 Vol. CO_2 equal to	Total Contraction, C $=(c+CO_2)$.	In Terms of Total Contraction, C.
Hydrogen.	$2H_2+O_2=2H_2O$ $\underbrace{2\text{ Vol.}+1\text{ Vol.}}_{3\text{ Vol.}}\ 0\text{ Vol.}$	$\boxed{H_2}\ \boxed{H_2}\ \boxed{O_2}\ =$	$\frac{1}{2}$ Vol. of H	3 Vol.	2 Vol. H	$\frac{2}{3}c=H$	...	3 Vol.	$\frac{2}{3}C=H$
Carbon Monoxide.	$2CO+O_2=2CO_2$ $\underbrace{2\text{ Vol.}+1\text{ Vol.}}_{3\text{ Vol.}}=2\text{ Vol.}$	$\boxed{CO}\ \boxed{CO}\ \boxed{O_2}\ =\ \boxed{CO_2}\ \boxed{CO_2}$	$\frac{1}{2}$ Vol. of CO	1 Vol.	2 Vol. CO	$2c=CO$	1 Vol. CO	3 Vol.	$\frac{2}{3}C=CO$
Methane.	$CH_4+2O_2=CO_2+2H_2O$ $\underbrace{1\text{ Vol. }2\text{ Vol.}}_{3\text{ Vol.}}=\underbrace{1\text{ Vol. }0\text{ Vol.}}_{1\text{ Vol.}}$	$\boxed{CH_4}\ \boxed{O_2}\ \boxed{O_2}\ =\ \boxed{CO_2}$	2 Vol. of CH_4	2 Vol.	1 Vol. CH_4	$\frac{1}{2}c=CH_4$	1 Vol. CH_4	3 Vol.	$\frac{1}{3}C=CH_4$
Ethane.	$2C_2H_6+7O_2=6H_2O+4CO_2$ $\underbrace{2\text{ Vol.}+7\text{ Vol.}}_{9\text{ Vol.}}=4\text{ Vol.}$	$\boxed{C_2H_6}\ \boxed{C_2H_6}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ =\ \boxed{CO_2}\ \boxed{CO_2}\ \boxed{CO_2}\ \boxed{CO_2}$	$\frac{7}{2}$ Vol. of C_2H_6	5 Vol.	2 Vol. C_2H_6	$\frac{2}{5}c=C_2H_6$	0·5 Vol. C_2H_6	9 Vol.	$\frac{2}{9}C=C_2H_6$
Ethylene.	$C_2H_4+3O_2=2CO_2+2H_2O$ $\underbrace{1\text{ Vol.}+3\text{ Vol.}}_{4\text{ Vol.}}=2\text{ Vol.}$	$\boxed{C_2H_4}\ \boxed{O_2}\ \boxed{O_2}\ \boxed{O_2}\ =\ \boxed{CO_2}\ \boxed{CO_2}$	3 Vol. of C_2H_4	2 Vol.	1 Vol. C_2H_4	$\frac{1}{2}c=C_2H_4$	0·5 Vol. C_2H_4	4 Vol.	$\frac{1}{4}C=C_2H_4$

Gaseous Mixtures with Two or Three Combustible Gases.

If methane and carbon monoxide are both present, neither of them alters their volume by oxidation to carbon dioxide, so that the following relation holds :—

$$1 \text{ vol. } CO_2 = 1 \text{ vol. } CO, \text{ or } 1 \text{ vol. } CO_2 = 1 \text{ vol. } CH_4.$$

A contraction results, however, owing to the oxygen taken up in the combustion, which must be subtracted from the contraction c, to obtain the nett contraction due to hydrogen.

(*a*) **Hydrogen and Carbon Monoxide.**—To the volume of carbon monoxide as ascertained (=vol. of CO_2 formed) there corresponds a contraction, due to the disappearance of oxygen, equal to half the volume of the CO_2. This must be subtracted from the contraction c, as found, in order to obtain the contraction due to hydrogen. The volumetric relations are therefore :—

$$CO = CO_2$$
$$\text{and} \quad H = (c - \tfrac{1}{2}CO_2)\tfrac{2}{3}.$$

Example (Mixture of Hydrogen, Carbon Monoxide, and Nitrogen) :—

Volume of Gas mixture	=	21.1 c.c.
,, Air added	=	97·5 ,,
Total	.	118.6 c.c.

After combustion = 102·1 c.c.; contraction c = 16·5 c.c.; H = 9·53 c.c.

After CO_2 absorption = 97·7 c.c.; carbon dioxide = 4·4 c.c.; CO = 4·4 c.c.

If, after absorbing the CO_2 formed in the combustion, the total contraction C ($=c+CO_2$) be considered, the volume of CO, of course, remains the same (= vol. of CO_2).

On the other hand, the volume of $H = \tfrac{2}{3}C - CO_2$.

Since, according to the first equation,

$$H = (c - \tfrac{1}{2}CO_2)\tfrac{2}{3}$$
$$\text{and} \quad C = c + CO_2$$
$$c = C - CO_2$$
$$\text{therefore :—} H = (C - CO_2 - \tfrac{1}{2}CO_2)\tfrac{2}{3} = (C - \tfrac{3}{2}CO_2)\tfrac{2}{3} = \tfrac{2}{3}C - CO_2.$$

Applying this to the example :—

Contraction	=	16.5 c.c.			
Carbon dioxide	=	4.4 ,,	CO	=	4.4 c.c.
Total contraction C	=	20.9 c.c.	H	=	9.53 ,,

In mixtures containing hydrogen and either carbon monoxide or

methane, provided that the total volume V of the combustible gases is known, the calculation on the basis of the foregoing is much simplified, since the volume of carbon monoxide or methane is equal to the ascertained volume of carbon dioxide, whilst the difference is due to hydrogen :—

$$\begin{aligned} CO \text{ or } CH_4 &= CO_2 \\ H &= V - CO_2. \end{aligned}$$

(*b*) **Hydrogen, Carbon Monoxide, and Methane.**—The volume of these constituents can be calculated if their total volume V (combustible portion) is known, a value which, in technical gas mixtures, is obtained from the estimation of the accompanying ingredient, nitrogen. The calculation starts from the known nitrogen content, N_1 of the air added for the combustion—*i.e.*, the volume of air × 0·7905. After combustion, followed by the absorption of the carbon dioxide, and of the excess of oxygen added from the air, there remains a volume of nitrogen, N_2, which is at least as large as N_1. The difference, $N_2—N_1$, gives the nitrogen, N, present in the original volume taken, R, whence the volume of the combustible gases is :—

$$V = R - N.$$

It then follows, as already shown, that—

$$\begin{aligned} H &= V - CO_2, \\ CO &= \tfrac{1}{3}CO_2 + V - \tfrac{2}{3}C \\ \text{and} \quad CH_4 &= (CO_2 + c)\tfrac{2}{3} - V. \end{aligned}$$

Starting again from the total contraction C, and substituting the equivalent value $(C - CO_2)$ for *c* in the above equation, the following simplified equations are obtained :—

$$\begin{aligned} H &= V - CO_2 \\ CO &= CO_2 + V - \tfrac{2}{3}C \\ CH_4 &= \tfrac{2}{5}C - V. \end{aligned}$$

Or, by adopting the following notation,

Volume I. = Gas residue (R) + air.
,, II. = Residue after explosion.
,, III. = Residue after explosion and absorption of CO_2.
,, IV. = Residue after absorption of the excess O.

Then :—

$$\begin{aligned} C &= \text{Vol. I.—Vol. III.} \\ CO_2 &= \text{,, II.— ,, III.} \\ N_2 &= \text{,, IV.} \\ N &= N_2 - N_1 (N_1 = \text{air} \times 79.05). \\ V &= R - N. \end{aligned}$$

(*c*) **Methane and Ethane.**—When the gaseous mixture contains higher homologues of methane, calculations are more complex. In

a mixture of hydrogen, carbon monoxide, methane, and ethane, the hydrogen and carbon monoxide are first removed by absorption with Paal's colloidal palladium solution (p. 244), and ammoniacal cuprous chloride solution respectively, or may be together determined by a process of fractional combustion at about 300° (see p. 261), the resulting carbon dioxide being absorbed. Methane and ethane can then be determined by combustion at about 900° with subsequent absorption of the carbon dioxide (see p. 294).

From the table on p. 249 it is seen that methane gives its own volume of CO_2 and a total contraction of twice its volume, whilst ethane gives twice its volume of CO_2 and a total contraction of 2·5 times its volume. If x and y represent the volumes of methane and ethane respectively, then :—

$$x + 2y = \text{vol. } CO_2 \text{ formed } (CO_2)$$
$$2x + 2.5y = \text{Contraction (C).}$$

Hence,
$$CH_4 = \tfrac{4}{3}(CO_2 - \tfrac{5}{4}C).$$
$$C_2H_6 = \tfrac{2}{3}(2C - CO_2).$$

In coal gas with the carbonising temperatures now usually employed, very little, if any, ethane is generally present, but with lower carbonising temperatures, and also when oil gas and carburetted water gas are added, appreciable amounts of ethane are often contained in the gas.

(*d*) If *more than two paraffins* are present in a gaseous mixture, the respective quantities cannot, in general, be determined. It may be noted that, on explosion, a mixture of one volume of methane and one of butane would behave in exactly the same manner as two volumes of propane. The nature of the paraffin constituents of such gaseous mixture can be estimated from the ratios of the contraction of volume on complete combustion to the volume of carbon dioxide produced on complete combustion and to the oxygen used up in the explosion. For the paraffins these ratios are as follows :—

	Contraction on Complete Combustion.	
	Volume of CO_2 produced.	Oxygen.
Methane	2·000	1·000
Ethane	1·250	0·714
Propane	1·000	0·600
Butane	0·875	0·531
Pentane	0·800	0·500

Burgess and Wheeler[1] ascertained the nature of the paraffins derived from the distillation of coal by calculating the number of CH_2

[1] *J. Chem. Soc.*, 1914, 105, 133.

groups present in unit volume of the mixed paraffins in the following manner. Consider a volume V of a mixture of paraffins to consist of mCH_4 groups and nCH_2 groups.

The complete combustion of a volume V of the mixture is represented by the equation:—

$$(mCH_4 . nCH_2) + (2m + 1.5n)O_2 = (m+n)CO_2 + (2m+n)H_2O.$$

$$\text{Hence, contraction on complete combustion} = m + 2m + 1.5n - (m+n).$$

$$= 2m + 0.5n.$$

$$= c$$

$$CO_2 \text{ produced} = m + n.$$

$$\text{Solving these equations we obtain } m = \frac{2c - CO_2}{3}$$

$$n = \frac{2(2CO_2 - c)}{3}.$$

And hence $\frac{n}{m} = \frac{4CO_2 - 2c}{2c - CO_2}$; and as each molecule contains one CH_4 group, m is numerically equal to V so that this expression also $= \frac{n}{V}$, the number of CH_2 groups per unit volume.

The nature of the olefines in a mixture may be estimated approximately by exploding a separate sample and subtracting the volume of carbon dioxide accounted for by other constituents from the total carbon dioxide produced.

Methods of Combustion.

(*a*) **Explosion.**—The simplest method of combustion consists in the explosion of the combustible mixture either with pure oxygen or with air, but it is not always practicable. As the explosion vessel, either a measuring burette provided with platinum electrodes is used, or a special explosion pipette. Water is quite unsuitable as the confining liquid if the carbon dioxide formed has to be determined, as under the high pressure of explosion a portion of this gas is dissolved; in most forms of apparatus the combustion is effected over mercury.

The explosion pipette, filled with water, devised by Pfeiffer (Fig. 132), obviates the absorption of the carbon dioxide in the following way. The liquid (0·1 per cent. sulphuric acid) in the explosion bulb A is drawn over into B before explosion; two stopcocks, *a* and *b*, are provided for this purpose.

This pipette is particularly suitable to the analysis of coal gas by Pfeiffer's method; it is of much smaller capacity than other forms of explosion pipettes, but will take one filling of the burette with air in addition to the combustible gas residue. The stopcock *a*, at the entrance to the bulb, instead of the customary rubber tubing and clip,

prevents risks due to back pressure, and in this respect the smaller capacity is also an advantage. By fixing the platinum electrodes in the position shown, the formation of drops of liquid between the points is avoided.[1]

The liquid is drawn into the bulb B, by means of a piece of rubber tubing 20 cm. long attached to the end of that bulb. Too large an excess of oxygen or air should not be used for the combustion. In calculating roughly beforehand the quantities necessary, the ratios given in the table on p. 249 are to be borne in mind, five volumes of air being used for each volume of oxygen required.

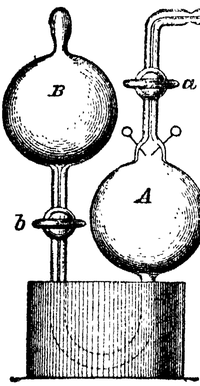

FIG. 132.

Below certain limits small quantities of combustible gases in presence of comparatively large quantities of indifferent gas do not undergo combustion. Explosion can then only be effected by the addition of oxygen, and it may even be necessary to add electrolytic gas in order to secure an explosive mixture. In practical work this complication has rarely to be resorted to, as the difficulty can be overcome by simpler methods, which will be explained subsequently.

On the other hand, in dealing with highly explosive mixtures, the nitrogen in the gases may also be oxidised, as was first pointed out by Bunsen. His experiments had reference only to admixtures of electrolytic gas and nitrogen, but he concluded that in order to avoid the oxidation of the nitrogen in the combustion of gaseous mixtures generally, not more than 26 to 64 vols. of combustible gas (inclusive of the necessary oxygen) should be present for every 100 vols. of incombustible mixture. These ratios form a satisfactory guide in the analysis of coal gas.

In any case, when the gases before explosion are under a pressure of about half an atmosphere, the ratio of the oxygen added to the volume of combustible gas should be approximately that indicated in the following table:—

Gas.	$\frac{\text{Volume of Oxygen.}}{\text{Volume of Combustible Gas.}}$
Hydrogen	1·5
Carbon monoxide.	1·5
Methane	5
Gases containing two atoms of carbon in the molecule, *e.g.* Ethane, C_2H_6	10
Gases containing three atoms of carbon in the molecule, *e.g.* Propane, C_3H_8	18
Gases containing four atoms of carbon in the molecule, *e.g.* Butane, C_4H_{10}	25

[1] Cf. *Chem. Zeit.*, 1904, **28**, 686.

Further details concerning the necessary addition of oxygen and the pressure at which the explosion is best carried out are given by Thomas.[1]

Preparation of Oxygen for Purposes of Combustion. Oxygen for analysis by explosion is conveniently prepared by gently heating pure potassium permanganate or perchlorate in a small, round bottomed flask or tube. About 2 g. of potassium permanganate or perchlorate is so heated, and care taken that all air has been cleared from the flask or tube before connection is made with the analysis apparatus. The oxygen should preferably be passed through caustic soda solution to remove any carbon dioxide formed by the combustion of dust, and to arrest any permanganate dust carried forward with the gas stream. The oxygen may be stored conveniently in a vessel over glycerine or brine.

Before the gas is used, its purity should be tested and at least 99·5 per cent. of the gas should be absorbable in alkaline pyrogallate solution.

(*b*) **Combustion without Explosion by means of Palladium.**—Hydrogen and carbon monoxide are easily oxidised with air when passed over heated palladium; methane does not take part in the combustion so long as the temperature is not raised too high. The method is, therefore, useful for the estimation of hydrogen and carbon monoxide in the presence of methane (fractional combustion); it gives satisfactory results with small amounts of these gases in the presence of large quantities of indifferent gases. The palladium is used either in the form of wire or of palladium asbestos, and is placed in a small capillary glass tube which is interposed between the measuring burette and a pipette filled with water or a second burette. The mixture to be burnt is passed over the heated palladium, and both the contraction and the carbon dioxide formed by combustion measured.

The exact temperatures to which the palladium must be raised has been the subject of considerable controversy. Winkler[2] asserts that methane is not burned at all when passed over palladium asbestos heated by a naked flame; even when considerable excess of easily combustible gases is present, at most only a trace of methane is burned. If the temperature rises too much, a little methane is burned as well. Hempel[3] considers that methane when passed over palladium asbestos does not burn at all at temperatures up to 100°. Combustion of methane commences at about 200°, and above this temperature a portion of the methane is burnt along with any hydrogen present in the gaseous mixture. According to Phillips,[4] the temperature of oxidation of methane by palladium asbestos is 404° to 414°, and

[1] *J. Chem. Soc.*, 1879, **35**, 213.

[2] See Lunge, *Tech. Gas Analysis*, 1914, p. 67.

[3] *Methods of Gas Analysis*, 1892, p. 134.

[4] *Amer. Chem. J.*, 1894, **16**, 163.

a variation in the relative proportions of inflammable gas and air appears to be without effect upon the oxidation temperature. Richardt[1] found that appreciable oxidation in the presence of palladium asbestos did not occur at temperatures below 600°, and that for the fractional combustion of hydrogen the temperature must not exceed 500° to 600°. Denham[2] states that the temperature of combustion of practically pure methane and oxygen lies between 514° and 546°. Any variation in the ratio of the volumes of the methane and oxygen tends to raise the combustion temperature above that necessary for the complete combustion of a mixture containing the two gases in the exact ratio required for complete combustion. The method of fractional combustion of hydrogen in the presence of methane using palladium asbestos is capable of affording reliable results provided the temperature does not exceed 500° to 550°. In no case was Denham able to effect anything approaching complete combustion of methane, although in some cases the temperature was as much as 100° above the temperature of combustion of methane. Richardt found only 1·3 per cent. of methane burnt at 600°.

Palladium wire, first recommended by Bunte,[3] is used as a very

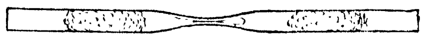

FIG. 133.

thin filament, about 1·5 cm. long, bent in two, and placed in the middle, narrowed portion of a tube of potash glass (Fig. 133); the wider parts of the tube are lightly stopped with asbestos fibre as a security against a possible explosion. The palladium is heated either by a spirit-lamp or by a very small gas burner. According to Richardt,[4] the heating must only be carried so far that the tip of the flame begins to be coloured yellow by the sodium of the glass; if this condition be fulfilled, the combustion of methane does not take place.

Palladium asbestos, which was introduced by C. Winkler for fractional combustion, is prepared in the following way. Palladium chloride, obtained from 1 g. of palladium, is reduced by the addition of a few c.c. of a cold, saturated solution of sodium formate, and sufficient sodium carbonate to make it strongly alkaline, and about 1 g. of best long-fibred asbestos is placed in the solution; this should absorb all the liquid. The damp mass is allowed to dry at a gentle heat, and in this way palladium in a very fine state of division is precipitated on the fibres, and adheres well to them even

[1] *J. Gasbeleucht.*, 1904, 47, 566 and 590.
[2] *J. Soc. Chem. Ind.*, 1905, 24, 1202.
[3] *J. Gasbeleucht.*, 1878, 21, 263.
[4] *Ibid.*, 1904, 47, 592.

when thoroughly dried on the water-bath; the asbestos is finally washed with boiling water and again well dried. The combustion capillary, which is from 5 to 10 cm. long, and about 1 mm. internal and 5 mm. external diameter, is filled by moistening a few threads of the asbestos with water, twisting them together on a piece of filter paper, and then sliding a piece about 1 cm. long into the middle of the tube; the capillary is then dried on the water-bath.

The combination of oxygen with hydrogen or with carbon monoxide takes place more readily by means of palladium asbestos than with palladium wire. If the gas be passed sufficiently quickly through the tube after the combustion has been started, the oxidation continues without further heating, and is seen by the glowing of the end of the asbestos thread next to the entering gases.

(*c*) **Combustion without Explosion by Means of Platinum.**—Platinum may be employed in place of palladium to accelerate the combustion of such gases as hydrogen, carbon monoxide, and methane. The platinum may be used in the form of wire or of a capillary tube. Methane is completely oxidised when passed with oxygen over brightly glowing platinum.

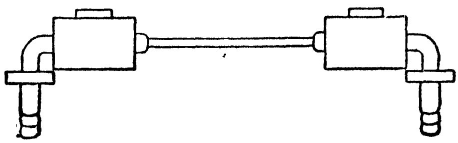

FIG. 184.

(1) *Winkler's Modification of the Hempel Pipette.*[1] A spiral of platinum wire which can be maintained electrically in an incandescent state is introduced into the ordinary form of Hempel pipette (p. 265). Contact between the gaseous mixture and the spiral is not very intimate, and an explosion is very liable to occur unless the mixture is led very slowly into the pipette.

(2) *Drehschmidt's Platinum Capillary Tube*[2] (Fig. 134). This consists of a seamless platinum tube, 20 cm. long, 2 mm. thick, and 0·7 mm. internal diameter, containing three or four pieces of platinum wire; the pieces of brass tubing soldered to the ends of the platinum tube serve for connecting to the measuring tube and pipette. Two small cooling cylinders, also made of brass, are fixed on to the brass tubes, just above the bend. The tube must be tested before use, to make sure that it is air-tight.

(3) *Levy's Silica-Platinum Combustion Capillary* is shown in Fig. 135. AB is a tube of fused silica, about 7 mm. external diameter and 1·5 mm. bore. CD is a wire composed of an alloy of platinum with 30 per cent. of iridium. This is stretched axially along the silica tube AB. The leading-in wires EC and FD are of molybdenum, this being the only metal that can be fused into silica satisfactorily. The molybdenum wires terminate at E and F in solid lumps of lead to which copper

[1] *Z. anal. Chem.*, 1889, **28**, 269; *J. Soc. Chem. Ind.*, 1889, **8**, 570. [2] *Ber.*, 1888, **21**, 3245.

wires are soldered. G and H are leading-in tubes of silica about 1 mm. bore, which serve to pass the gas over the wire CD which is heated by a current from a 2- or 4-volt battery, the temperature of the wire being adjusted by means of a rheostat included in the circuit. The wire is

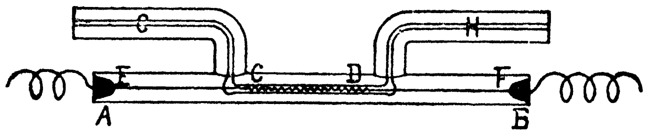

FIG. 135.

corrugated so as to take up the expansion on heating. This may also be effected by using a straight wire and employing a short spring of molybdenum. The oxidation of a gaseous mixture is accelerated if the wall of the capillary is coated with finely divided platinum by spluttering of the platinum wire.

While the limitations accompanying the use of platinum in the fractional combustion of gaseous mixtures have not been specified with the same precision as for palladium (p. 255) or for cupric oxide (p. 261), the method gives reliable results when used for methane determinations. Levy[1] asserts that by the use of the silica-platinum capillary tube, an accurate analysis can be made of a mixture containing hydrogen, carbon monoxide, methane, and nitrogen. Two methods are proposed :—

(i) *Complete Combustion Method.* A few cubic centimetres of the mixture, after the removal of the absorbable constituents, together with excess of air or oxygen, are measured and then passed through the oxidation tube, the temperature of which is regulated to incipient whiteness. By excess of air is meant (say) nine times the gas volume. This operation is repeated once or twice, until no further contraction is observed, and the maximum contraction noted. The gas is then passed into a potash pipette to remove the carbon dioxide produced by the combustion, and the further contraction is noted. The excess of oxygen is then absorbed with alkaline pyrogallol, thus giving a measure of the amount of oxygen required for the combustion. [This, of course, pre-supposes a knowledge of the amount of oxygen added, which is known from the composition of the gas added.]

Let the volume of carbon monoxide be x.
" " methane be y.
" " hydrogen be z.

Then C_1 = contraction $= \frac{x}{2} + 2y + \frac{3}{2}z$.

" C_2 = contraction in potash $= x + y$.

" V_0 = oxygen used $= \frac{x}{2} + 2y + \frac{z}{2}$

[1] *J. Gas Lighting*, 1913, **122**, 457.

Solving these three equations for x, y, and z, we have :—

$$x = \text{carbon monoxide} = \frac{4C_2 + C_1 - 3V_0}{3}$$

$$y = \text{methane} = C_2 - x$$

$$\left(\text{or } y = \frac{3V_0 - C_1 - C_2}{3}\right)$$

$$z = \text{hydrogen} = C_1 - V_0$$

(ii) *Fractional Combustion Method.* By regulating the temperature of the heated wire, the hydrogen, carbon monoxide, and methane can also be determined by fractional combustion. If the wire be heated to scarcely visible redness, the hydrogen, and occasionally some of the carbon monoxide, is burnt, while the methane remains unaffected. On increasing the temperature to incipient whiteness, the remainder of the carbon monoxide and the whole of the methane are oxidised. The advantage of this method of working is that the accuracy of the determination of the combustible gases is increased, and the necessity for the determination of the oxygen consumed is obviated. The method of working is as follows: The gaseous mixture is passed over the wire (which is heated to scarcely visible redness) a few times until no further contraction is observed. The gas is then passed into potash, and the amount absorbed, if any, is noted.

Let the contraction be C_1 and the further contraction on passing into potash be C_2. Then the carbon monoxide oxidised at this stage $= C_2$. The contraction due to carbon monoxide $= \frac{C_2}{2}$. Hence the contraction due to hydrogen $= C_1 - \frac{C_2}{2}$ and hydrogen $= \frac{2}{3}\left(C_1 - \frac{C_2}{2}\right)$. After heating to whiteness, let the further contraction observed be C_3, and the contraction on passing into potash be C_4. Let the remainder of the carbon monoxide be x and the methane be y. Then $C_3 = \frac{x}{2} + 2y$ and $C_4 = x + y$. Hence $y = \text{methane} = \frac{2C_3 - C_4}{3}$, and $x = \text{carbon monoxide} = C_4 - \text{methane}$.

$$\text{Hence hydrogen} \quad = \frac{2}{3}\left(C_1 - \frac{C_2}{2}\right)$$

$$\text{methane} \quad = \frac{2C_3 - C_4}{3}$$

$$\text{carbon monoxide} \quad = \frac{C_2}{2} + C_4 - \text{methane.}$$

Usually it will be found that no contraction is observed on passing into potash after the first combustion—*i.e.*, $C_2 = 0$; but C_2 should be determined as a check, in case some carbon monoxide should be oxidised together with the hydrogen.

The complete combustion method is more rapid than the operation described, as only one combustion and absorption in potash are required. On the other hand, however, it entails a measurement of the oxygen, which the fractional method does not. The complete combustion method is most suitable for use in a constant volume apparatus; whereas in instruments in which measurements are made at constant pressure, the fractional combustion method is far preferable.

(*d*) **Fractional Combustion employing Cupric Oxide.**—This method, which is due to Jaeger,[1] depends on the fractional combustion of the mixture of gases in the presence of cupric oxide at various temperatures. As the oxygen required for the combustion is not added in the gaseous form, the volume changes are very simple; thus, the hydrogen disappears completely on burning and its volume is equal to the contraction, whilst the methane forms an equal volume of carbon dioxide, which is easily measured by absorption. The combustion tube, of the form shown in Fig. 136, is made of hard Jena glass with a capillary on one side and a somewhat wider tube on the other. Large-grained copper oxide is introduced so that it lies at the beginning of the

Asbestos. Asbestos.

FIG. 136.

capillary, and a plug of asbestos fibre is placed against it; the wide part of the tube is then filled with freshly ignited powdered copper oxide, kept in position by a second plug of asbestos. The tube is connected by rubber tubing on one side with the measuring burette, and on the other side with the absorption pipette charged with potassium hydroxide solution. For the combustion of the hydrogen the tube is heated to 250°, as shown by a thermometer, the bulb of which is placed against the tube. After oxidising the hydrogen and reading the contraction, the thermometer is removed and the methane then oxidised by heating the copper oxide to a red heat. As the carbon dioxide formed is absorbed by the potassium hydroxide in the pipette, the contraction gives the volume of the methane directly.

The air enclosed in the tube takes part in the combustion of the hydrogen; the correction necessary for the oxygen thus removed is determined once for all, so that it can be applied in all the estimations. It may amount to about 0·8 c.c.

The combustion with copper oxide has the great advantage that the whole of the gas left after absorption can be taken for the determination, so that any errors do not influence the final result to the same

[1] *J. Gasbeleucht.*, 1898, **41**, 764.

extent as when only a fraction of the residue is used. A disadvantage arises from the difficulty in burning the methane completely and from the high temperatures necessary for the combustion, as the tube must be allowed to cool down before reading off the volume; the copper oxide must also be reoxidised after each analysis. Further details are given under the description of Jaeger's method of gas analysis (p. 293). This method, however, is frequently employed for the determination of the percentage of nitrogen only in gases; the percentage of nitrogen obtained in this way is more accurate than that found by the explosion method, in which it is always taken by difference, and is, therefore, subject to the combined errors in the determination of all the other constituents.

The accuracy of this method of fractional combustion is dependent upon the assumption of complete oxidation of the respective constituents. This has been investigated by Terres and Mauguin,[1] whose apparatus consisted of a spiral of Jena glass having an internal diameter of 10 mm. and a length of 80 cm. The spiral was packed with cupric oxide and heated to the desired temperature in a bath of potassium and sodium nitrates. They reached the following conclusions:—

(1) *Carbon Monoxide.* Dry carbonic oxide when not mixed with other combustible gases is never completely burned at the usual temperature of fractional combustion. Even in a mixture containing a large proportion of carbonic oxide, quite erroneous results may be obtained at the customary temperatures. At a red heat the combustion of carbonic oxide is complete. Alone, and dry, 90 to 94 per cent. of the gas is burnt at 305°.

(2) *Hydrogen.* The combustion of hydrogen commences at 160° to 170°, and is complete at 250°.

(3) *Carbon Monoxide and Hydrogen.* The presence of hydrogen is known to reduce the temperature of combustion of carbonic oxide and of other gases, and owing to this fact carbonic oxide in the presence of small quantities of hydrogen is completely burned at lower temperatures than when hydrogen is absent. It seems possible to secure complete quantitative fractional combustion of a carbonic oxide-hydrogen mixture without combustion of methane by cupric oxide at 300°, provided the mixture contains approximately equal proportions of carbon monoxide and hydrogen on the one hand, and methane on the other.

(4) *Methane.* The combustion of methane over cupric oxide begins at 310°. When methane is present in very small proportion, the combustion is not quite complete even at a red heat. In high concentration, methane is completely burned at a red heat.

(5) *Hydrocarbons* such as acetylene, ethylene, and benzene are not

[1] *J. Gasbeleucht.*, 1915, **58**, 8; also *J. Gas Lighting*, 1915, **129**, 257.

burnt quantitatively at 300°, even in the presence of hydrogen, owing to the deposition of carbon.

Jaeger employed the cupric oxide in the form of powder. Taplay[1] used a rod of the oxide supported on silica loops so as to lie axially within a fused silica combustion tube. J. P. Wibaut[2] remarks that the end point of the oxidation is not easily detected, as the reaction between cupric oxide and hydrogen or methane is slow, and the slight diminution of volume due to oxidation may be masked by the expansion after passing over the heated oxide. He accordingly recommends that the reaction be accelerated by using a greyish-white mixture of cupric oxide and cerium dioxide.

Determination of Carbon Monoxide by Means of Iodine Pentoxide.—The oxidation of carbon monoxide by iodine pentoxide was independently introduced by Gautier[3] and Nicloux[4] for the accurate determination of this gas in air. The following represents the reaction occurring: $5CO + I_2O_5 = 5CO_2 + I_2$.

The quantitative determination is made either by ascertaining the iodine liberated or the carbon dioxide formed.

According to Nicloux, the gas is first passed through a U-tube containing small pieces of potash, then over pumice soaked in sulphuric acid, and finally through a U-tube containing iodine pentoxide immersed in an oil-bath at 150°. An absorption tube containing 10 c.c. of sodium hydroxide is used for absorbing the carbon dioxide formed and the iodine liberated. The air is aspirated at a rate not exceeding 10 c.c. per minute. The iodine is liberated from the potash by the addition of a little sodium nitrate and sulphuric acid, and extracted with carbon bisulphide or chloroform. The coloration produced is compared with that of a standard prepared by treating a solution of potassium iodide containing 0·1 mg. per c.c. with sodium nitrate and sulphuric acid, and similarly extracting with carbon bisulphide or chloroform. The iodine liberated can likewise be very accurately determined by titration against *N*/100 sodium thiosulphate solution.[5] The carbon dioxide produced may be determined by titrating the caustic soda solution against baryta water. It is pointed out by Gautier, that traces of ethylene and acetylene reduce the oxidation of carbon monoxide effected. Levy[6] has shown that this inhibitory effect is avoided by carrying out the oxidation at 170°, and he suggests that the inhibition is due to water produced by oxidation of ethylene, etc., and is prevented by keeping the temperature above that of dehydration of iodic acid. Spitta has discussed the method in detail.[7]

[1] *J. Gas Lighting*, 1918, 144, 870.
[2] *Chem. Weekblad*, 1914, 11, 498; *J. Gas Lighting*, 1914, 127, 174.
[3] *Comptes rend.*, 1898, 126, 793, 931.
[4] *Ibid.*, 746; 1912, 154, 1166.
[5] Kinnicutt and Sanford, *J. Amer. Chem. Soc.*, 1900, 22, 14.
[6] *J. Soc. Chem. Ind.*, 1911, 30, 1437.
[7] *Arch. f. Hygiene*, 46, 284.

A portable form of apparatus capable of giving results correct to 0·005 per cent. has been described by Graham.[1] The iodine liberated is absorbed in a solution of potassium or sodium iodide, and the solution titrated against standard thiosulphate solution.

Rideal and Taylor[2] describe an apparatus for recording the percentage of carbon monoxide in a stream of gas. This constituent is catalytically and preferentially oxidised to carbon dioxide, which is then absorbed by a stream of standard lime water. The electrical conductivity of the resultant solution is recorded, and serves to indicate the percentage of carbon monoxide in the gas stream. The apparatus is devised principally for recording the purity of the hydrogen used in ammonia synthesis.

Determination of Nitrogen.—Since no methods of technical value are available for the determination of nitrogen, either by absorption or by oxidation, the proportion present in gaseous mixtures is very commonly taken by difference. Data obtained in this way are inaccurate, as they bear the combined experimental errors of the other determinations, which may either cancel or augment each other.

A direct determination of nitrogen may be made in the residual gases of an analysis by absorbing the excess of oxygen with alkaline pyrogallol and measuring the volume of nitrogen left, provided the percentage of nitrogen in the measured volume of oxygen added for combustion has been previously ascertained. The experimental error in this method is, however, very considerable, especially when only a small volume of gas is taken for the combustion.

It is accordingly much preferable to make an independent determination of the nitrogen. This can be effected by complete combustion of the mixture with copper oxide, whereby the constituents other than nitrogen are removed and the residual gas measured. This determination is advantageously carried out either by the apparatus devised by Jaeger (p. 293) or by the "Metrogas" apparatus (p. 295).

APPARATUS FOR GAS ANALYSIS

A very great variety of apparatus has been designed for technical gas analysis which differ chiefly in the degree of accuracy with which they can be employed. The less accurate forms of apparatus are used chiefly for control purposes, and with careful manipulation give reliable comparable results. With these forms acidulated water is generally used as the confining liquid, so that errors arising from the solubility of the gases concerned are introduced. Corrections

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 10 T; see also *J. Chem. Soc.*, 1914, **105**, 1996.

[2] *Analyst*, 1919, **44**, 89-94.

for temperature and pressure are not usually made; owing to the analyses being carried out rapidly the changes in pressure are inappreciable; in many forms of apparatus changes in temperature are controlled by surrounding the measuring burette with a water-jacket. Simplicity of construction and easy manipulation are the chief considerations in the design of apparatus of this character.

For more accurate work, such as the complete analysis of heating and illuminating gas, more complex apparatus is employed, in which mercury is used as the confining liquid, and corrections for temperature and pressure are applied. The modern forms of such apparatus permit of sufficient rapidity in use to be applicable for technical purposes. Of the less accurate forms of apparatus, those of Hempel, Orsat, Bunte, Honigmann, and Pfeiffer will be described, and of the more accurate forms those of Bone and Wheeler and of Haldane, and in addition the apparatus of Jaeger and the "Metrogas" apparatus, which, as stated above, are especially applicable to the determination of nitrogen.

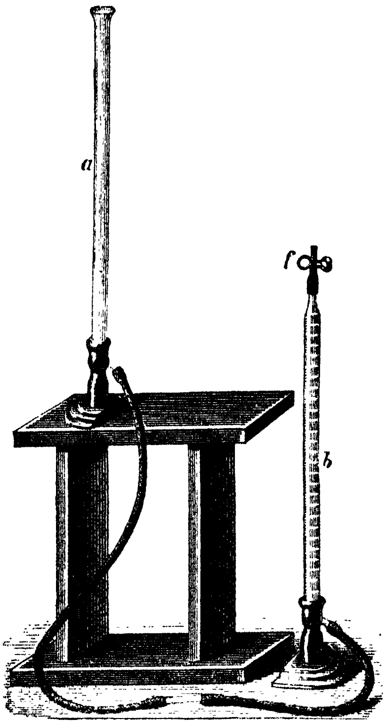

FIG. 187.

Whilst many other forms of apparatus have been constructed, the above may be regarded as representative of modern practice and applicable to the requirements of general technical gas analysis.

Apparatus designed for the "automatic" analysis of gases is described separately at the end of the section (p. 321 *et seq.*).

Hempel's Apparatus is extremely simple in construction and use, and in careful hands affords fairly accurate results; it is very adaptable, as Hempel has devised a variety of pipettes for special purposes, and is therefore much used.

The burette (Fig. 137) consists of a measuring tube *b*, graduated into 100 c.c. with 0·2 c.c. divisions, and the pressure tube *a*, each of which is contracted at the lower end and bent at right angles, so as to fit into slots in weighted wooden supports. The measuring tube is also contracted at the top, and terminates in a capillary tube ½ to 1 mm. in diameter and 3 cm. long. The tubes are connected by a piece of rubber tubing about 100 cm. long, preferably divided in the

middle, with the parts joined together by a short piece of glass tubing to facilitate the cleaning of the burette. A short piece of thick-walled rubber tubing, provided with a pinch-cock, is attached at *f*.

A better form of burette has the rubber connection and pinch-cock at *f* replaced by a three-way tap, of the form shown in Fig. 137A.

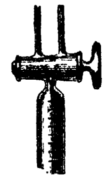

FIG. 137A.

Another modification, generally known as the modified *Winkler burette*, shown in Fig. 138, is provided with a simple gas tap at *a* and with a three-way tap at *b*; its chief advantage is in the analysis of mixtures containing an easily soluble gas, since the initial volume of gas can be measured without bringing it into contact with water, which is always used as the confining liquid in the various forms of Hempel burette employed for technical analysis.

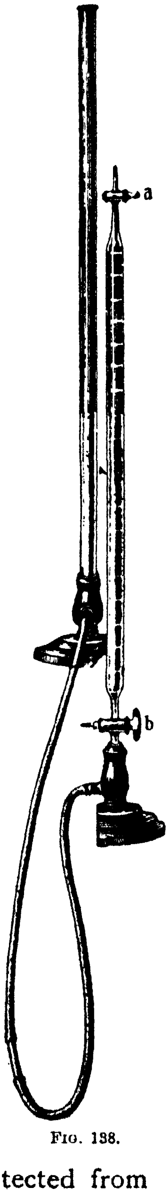

FIG. 138.

Any of these forms of burette may be provided with a water-jacket to minimise changes of temperature.

The pipettes, in which the various reagents for the absorption of the gases are contained, consist of two bulbs, *a* and *b* (Fig. 139), connected by the tube *d*, of which *b* is attached to a capillary tube *c* of ½ to 1 mm. diameter; a white porcelain plate, *m*, is fixed at the back of *c*, to render the thread of liquid in the capillary more visible. The capacity of the bulb *b* is about 150 c.c., that of *a* about 100 c.c. to allow a sufficient quantity of the absorbent to be left in *b* after the introduction of 100 c.c. of gas The pipettes are mounted either on wooden (Figs. 139 and 143) or on adjustable iron frames (Figs. 140, 141, 142, and 144). Pipettes for use with solid absorbents such as phosphorus, are provided with a cylindrical bulb, tubulated at the bottom (Fig. 141), and closed by a good rubber stopper; double pipettes (Figs. 142 and 143) are used for absorbents which require to be protected from the air, such as pyrogallol, or which evolve irritating fumes, such as bromine.

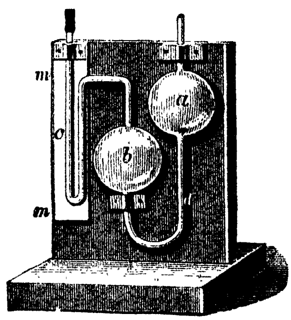

FIG. 139.

A good form of simple pipette, in which a small second bulb, filled with glass beads, is placed above the absorption bulb, is shown in Fig. 144.

The simple pipettes are filled by pouring the absorbent through the tube attached to the bulb *a* (Fig. 139), whilst the air is sucked out from *b*; sufficient liquid is introduced to fill the bulb *b* and the capillary tube *c* completely, and to leave a small quantity in *a*. To

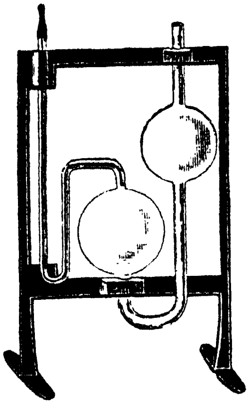

FIG. 140.

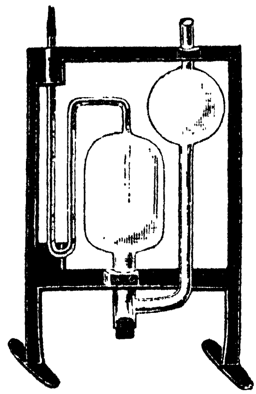

FIG. 141.

fill the double pipettes, the best plan is to attach a glass tube a metre long, and provided with a funnel, to the top of the capillary tube, and to pour the absorbent liquid in through this, until the first bulb is completely filled; to effect this without the liquid overflowing to the protecting bulbs *c* and *d* (Fig. 143), it is necessary to blow out the air

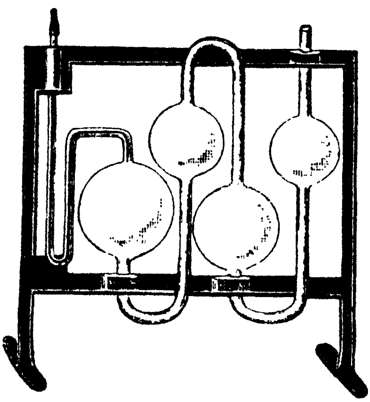

FIG. 142.

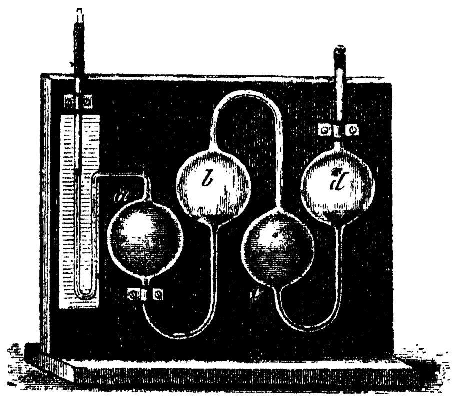

FIG. 143.

contained in *a* through the funnel several times, after a portion of the absorbent has been introduced. After *a* and the lower part of *b* have been filled, water is introduced into *d* and *c*, through the tube attached to *d*, after first blowing over a portion of the liquid in *a* into *b*, so as to remove the air in the latter.

The burette and pipettes are connected by a piece of thick-walled

capillary tubing of 1 mm. internal diameter and 18 cm. in length, as shown in Fig. 145, the pipette and burette being attached to it by stout rubber tubing.

To introduce gas for analysis into the burette, the pressure tube B (Fig. 145) is filled with water and then raised, so as to drive out the air in the measuring tube A, and the pinch-cock or tap at *f* closed. A 0·5 per cent. solution of sulphuric acid in water is used as the confining liquid; it is advantageous to keep a stock of this acidulated water so that it has attained the temperature of the laboratory before use. The gas supply is attached at *f*, and the sample syphoned in, by opening *f* and lowering the pressure tube. A little more than 100 c.c. of gas is drawn in and then *f* is closed. When the Winkler burette (Fig. 138) is used for the analysis of a mixture containing a very soluble constituent, the

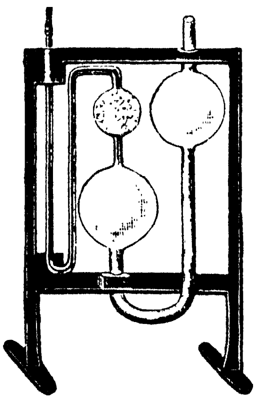

FIG. 144.

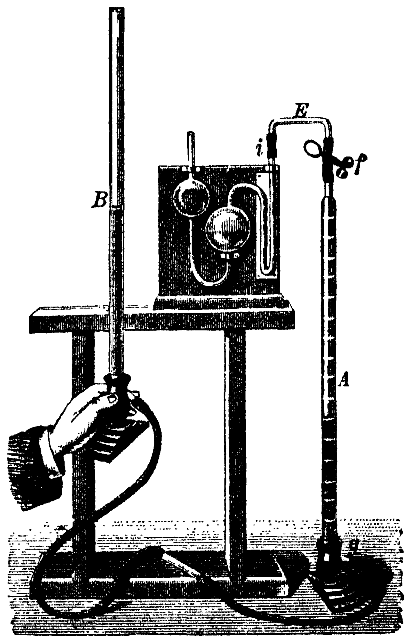

FIG. 145.

sample is introduced through the three-way tap *b*, at the bottom of the burette. To obtain exactly 100 c.c. of gas for analysis the pressure tube is raised gradually, and when the liquid stands exactly at the 100 c.c. graduation, the connecting rubber tube is closed by pressing it between the thumb and finger; *f* is then momentarily opened to establish the atmospheric pressure, and the volume verified by bringing the water in the two tubes of the burette to the same level.

The burette and the pipette are then connected, as shown in Fig. 145. To obviate the error due to the air in the capillary tube E, this is first connected to the pipette, and the absorbent liquid blown over from the latter until it begins to run out at the free end of the

capillary, which is at once attached to the burette; it is convenient to attach a piece of rubber tubing to the tube of the upper bulb of the pipette for this purpose. The gas is transferred from the burette to the pipette by raising the pressure tube and opening *f*; water is driven over to wash out the capillary tube of the pipette, as far as the top of the absorption bulb, so that the gas is confined between two surfaces of liquid, and *f* is then closed. The absorption is promoted by gently shaking the pipette; some recommend the removal of the capillary E, but sufficient movement can be given to the liquid without disconnecting. After absorption, the gas is syphoned back into the burette by lowering B, the liquid in the pipette being drawn over as far as the pinch-cock (or stopcock) at *f*; after allowing two minutes for the water in the burette to drain, the liquid in the two tubes of the burette is brought to the same level and the reading taken. The absorption is repeated until a constant value is obtained, and the decrease in volume, with each reagent, represents the percentage of absorbed gas present in the mixture. The capillary connecting tube E must be thoroughly cleaned from each successive reagent.

As the Hempel apparatus is not used for work of high accuracy, some workers prefer to avoid introducing the absorbents into the connecting capillary tube, and in transferring the gas from the burette to the absorption pipette, and in syphoning it back, bring the confining liquid only as far as the tap of the burette and the top of the capillary of the pipette respectively.

The Hempel apparatus can be used for the analysis of mixtures containing carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, nitrogen, olefines, and hydrocarbon vapours. The preparation of the various absorbents has been already described (pp. 241-247). The following will indicate the general mode of procedure.

(1) *Carbon dioxide* is determined by means of a solution of potassium hydroxide in a simple absorption pipette (Fig. 139).

(2) *Oxygen* is absorbed in an alkaline pyrogallol solution contained in a composite absorption pipette (Fig. 143), or by means of copper wire gauze immersed in concentrated ammonia contained in a tubulated pipette (Fig. 141). If desired, the oxygen can be absorbed, without previous absorption of carbon dioxide, by means of phosphorus under water in a similar pipette.

(3) *Carbon monoxide* is absorbed by an ammoniacal or acid solution of cuprous chloride contained in a composite absorption pipette (Fig. 143).

(4) *Hydrogen* is determined by combustion with oxygen either over palladium asbestos or by explosion. The former method is carried out by replacing the connecting capillary tube E (Fig. 145) by a similar

tube containing a thread of asbestos fibre coated with metallic palladium, as described on p. 256, and heated by a small spirit-lamp.

To introduce the fibre, a few loose strands are moistened with water and then rolled into a fine straight thread, which is slid into the capillary tube held vertically, and before it has been bent for attachment to the burette and pipette. The thread is easily brought into position in the centre of the tube; the water is then drawn off, by means of filter paper, the moisture removed by drying, and the ends of the tube bent at right angles for a length of 3·5 to 4 cm.

The capillary tube is attached on the one side to the burette in the usual way, and on the other, to a simple pipette filled with water. Not more than 25 c.c. of the gas in the burette is first passed over into the pipette, the necessary quantity of air (about 75 c.c. should suffice) then introduced into the burette, its volume measured and also the volume of gas+air, after syphoning back the former from the pipette, as a check. The whole is then mixed by passing it into the pipette, which is gently shaken; it is then passed backwards and forwards over the heated palladium asbestos till no further contraction occurs; two-thirds of this contraction is due to the hydrogen. The level of the confining liquid is brought to the bottom of the capillary combustion tube, in syphoning the gas to and from the burette. For the introduction of the air or oxygen, the burette with the three-way tap at the top (Fig. 137) is very advantageous, as it avoids disconnecting the capillary tube.

The method is very valuable for determining hydrogen in presence of methane (see p. 255). Carbon monoxide may be similarly determined, the carbon dioxide formed being subsequently absorbed by potassium hydroxide.

The Determination of Hydrogen by Absorption with Palladium. Hempel has worked out the conditions under which the well-known power possessed by palladium of absorbing hydrogen can be used for the determination of this gas.

Pure palladium is indifferent towards a mixture of hydrogen, methane, and nitrogen, but if a small proportion of palladious oxide is present, a partial combustion of the hydrogen occurs, and the heat thus generated is sufficient to ensure the absorption of the rest of the hydrogen present; the process is accordingly in part a combustion and in part an occlusion of the hydrogen.

The palladium is prepared by heating 4 to 5 g. of palladium sponge, in portions of 1 g. at a time, on the lid of a platinum crucible, until it nearly glows, and then allowing it to cool slowly, whereby a thin film of oxide is formed upon the surface of the metal. Four grams of this oxidised sponge is placed in a U-tube, of 4 mm. internal diameter and 20 cm. total length; the tube is placed in a

beaker, and kept at a temperature of 90° to 100° by hot water, as shown in Fig. 146.

The U-tube is attached on the one side to the burette, and on the other to a pipette charged with water, and the gas syphoned backwards and forwards three times; the beaker H is then replaced by one containing cold water, and the gas again passed twice through the tube, so as to cool it to the original temperature. The volume is finally adjusted by syphoning the liquid in the pipette to *i*, and the reading taken; the decrease in volume represents the absorbed hydrogen plus the volume of oxygen originally contained in the U-tube. The latter is determined, once for all, by closing one end of the U-tube with a glass stopper attached by a piece of rubber tubing, and then placing it in a beaker of water at 9°; the open end of the tube is then connected with the burette, previously filled with water, and the tube heated in the beaker to 100°. The increase of volume, as measured in the burette, is that due to an increase of 91° in temperature, and therefore equal to one-third of the volume of gas; from this value the volume of oxygen in the U-tube is obtained. The palladium is regenerated after use by first passing air over it, when it gets quite hot; any drops of water that may collect are removed, the palladium then shaken out of the tube and oxidised as before.

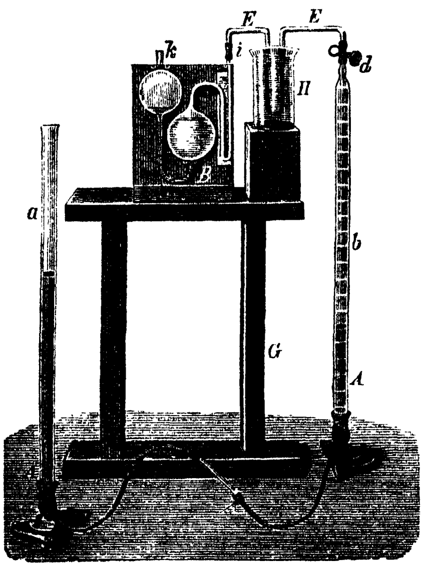

FIG. 146.

Carbon dioxide, oxygen, carbon monoxide, heavy hydrocarbons, and vapours of hydrochloric acid and of ammonia, prevent the determination of hydrogen by this method, and it is but seldom used in technical gas analysis. It has, however, the advantage that since no air is added, the volume of the gas that can be used for the analysis is not restricted.

Methane is determined by combustion with oxygen, either by explosion or by a heated platinum wire.

The Determination of Methane by Explosion. The Hempel explosion pipette is used for this method. The earlier form is shown in Fig. 147; it is a simple pipette, provided with electrodes at *k* and a stopcock at *d*, and is filled with water. An improved form of pipette, in which mercury is used as the confining liquid, is shown in Fig. 148; the bulb

of the ordinary pipette is attached to a levelling bulb by a stout piece of rubber tubing. A small stopcock fitted to the top of the capillary tube at *c* removes the risk of loss by leakage on firing.

The residual gas, after the determination of the hydrogen, is syphoned over into the explosion pipette, the necessary quantity of air or oxygen added, in the same manner as in the combustion of hydrogen over palladium asbestos, the total volume then measured as a check, and the whole passed over into the pipette, where it is mixed by gentle shaking; the water in the burette is syphoned over until the capillary tube of the pipette is filled, when the tap at *c* is closed. The pressure on the mixture is reduced slightly before firing by lowering the pressure bulb *a*; the tap *d* is then closed and the gases fired by attaching the terminals of a small Ruhmkorff coil to

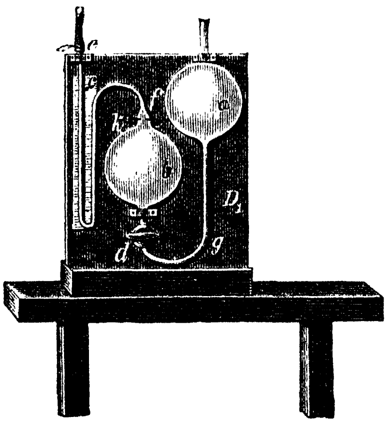

FIG. 147.

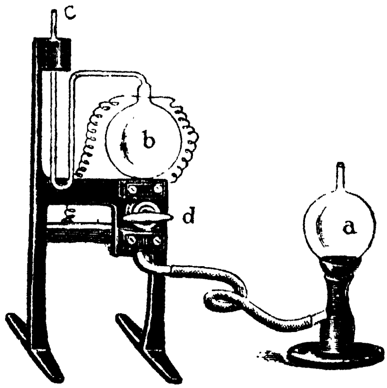

FIG. 148.

the electrodes of the pipette. After the combustion, the gas is syphoned back into the burette, and the carbon dioxide formed determined by absorption with potassium hydroxide.

With regard to the volume of air or oxygen to be added for the combustion (see p. 254), a ratio of 50 : 100 is a good working proportion, the oxygen theoretically required for the combustion of the methane being included in the combustible gases, the excess forming part of the incombustible gases. The choice of air or oxygen will accordingly be decided by the volume of gas to be dealt with and its methane content. Oxygen from ordinary oxygen cylinders can conveniently be used, the percentage of oxygen it contains having been previously determined.

Many of the absorption pipettes described above have been modified so that the gas enters the pipette below the surface of the liquid, but is drawn off from the top in the usual manner.[1]

[1] See, *e.g.*, Dennis, *J. Ind. Eng. Chem.*, 1912, 4, 12; Van Alstine, *ibid.*, 1919, 11, 51.

Orsat's Apparatus.—This form of apparatus is primarily due to Schlösing and Roland;[1] it has been modified and improved by Orsat,[2] Salleron, F. Fischer,[3] Lunge, Sodeau, and others, and is generally known as the Orsat gas analysis apparatus. The apparatus is primarily designed to combine rapidity with convenience in working.

Fischer's modification consists of a measuring tube or burette A (Fig. 149), surrounded by a water-jacket, which is attached at the top to absorption vessels, generally called pipettes, D and E, by means of capillary tubes, and at the bottom to a pressure bottle L. The whole is fixed in a case, which can be closed by sliding shutters for transport. The burette has a capacity of 100 c.c., the lower portion being graduated in tenths and the upper in whole c.c. The capillary tube, leading to the pipettes, is provided with a tap at each junction, as shown, and there is a mark *m*, on each of these, below the tap; the tap *c* is a three-way stopcock which allows of connection between the gas supply and the tube B, or between B and A, or between A and the outside air. The U-tube B is filled with cotton wool to retain any soot or dust from the gas sample. The pipettes are filled with bundles of glass tubes, so as to provide a large surface for contact between the gas and the absorbent; the open end of each pipette is closed by a rubber stopper carrying a glass tube, to which a thin rubber ball is attached to protect the contained liquids from contact with the air. To prepare the apparatus for use, the pressure bottle L is filled with water and then raised, so as to drive out the air in A, through the tap *c*. The pipette D

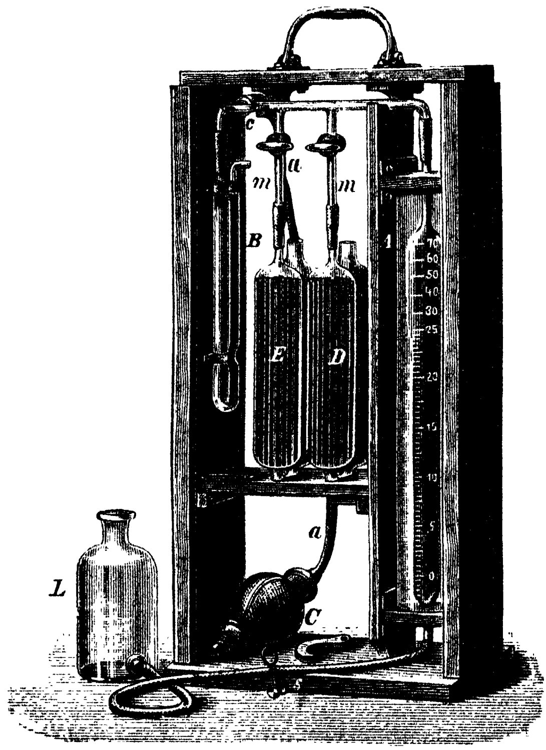

FIG. 149.

[1] *Ann. Chim. Phys.*, 1868, **14** [iv.], 55.
[2] *Annal. des Mines*, 1875, **8** [vii.], 485 and 501.
[3] *Fischer's Jahresber.*, 1880, **26**, 330.

is then filled with potassium hydroxide solution, and the pipette E with pyrogallol solution; a third pipette, charged with cuprous chloride solution, can be employed for the absorption of carbon monoxide. The absorbing liquids are poured in from the back, so as to fill about half of the pipette, and then drawn up to the mark *m*, by opening the tap of the pipette and lowering the pressure bottle L; when the liquid reaches the mark, the tap is closed and the back opening of the pipette closed by the thin rubber ball. Before proceeding with an analysis, the apparatus should first be tested to see whether it is air-tight, by filling the burette with water, then closing the tap *c* and lowering the pressure bottle, when it will at once be seen, from any change in level of the water in A, whether there is any leak.

To introduce the sample of gas, A is again filled with water and the tap *c* turned so as to communicate through B with the outside air. The rubber aspirator C, which is connected with the gas supply, is then attached to the exit tube of B; after clearing out the air in B by aspirating, the tap *c* is turned, so as to connect the gas supply with the burette, and the sample introduced by lowering the pressure bottle L. A little more than 100 c.c. of gas are syphoned into A, and the tap *c* then closed. To obtain exactly 100 c.c. for analysis, the gas is compressed to the zero mark by raising L, the rubber tube *s* then closed, either by the pinch-cock or by the fingers, and the tap *c* momentarily opened to the outside air, so as to establish atmospheric pressure on the contained gas.

To determine the carbon dioxide, the tap connected with D is opened and the gas in A transferred into the pipette, by raising the pressure bottle; this operation is repeated several times, alternately lowering and raising L, until the absorption is complete, the level of the liquid in D being finally adjusted to the mark *m*, the attached tap closed, and the reading in the burette taken, the pressure on the gas being adjusted to that of the atmosphere by raising L, so that the levels of the liquid in it and in the burette are the same. The reading gives the percentage of carbon dioxide directly. Oxygen is similarly determined in the pipette E. Cuprous chloride solution becomes unreliable for the determination of carbon monoxide after having been used for a short time (p. 244), and Fischer prefers to omit this determination in the analysis of furnace gases. Other forms of apparatus are, of course, available for the determination of this gas, and, as already pointed out (p. 231), its quantity can also be gauged approximately from the percentage of carbon dioxide and oxygen contained in such gases. Carbon monoxide does not occur nearly so frequently in furnace gases, in presence of free oxygen, as has been assumed to be the case, from inaccurate analyses.

When the analysis is completed, the residual gas is cleared out of the burette and the apparatus is then again ready for use; an analysis can be completed in five minutes, with an accuracy of 0·2 per cent. When exhausted, the contents of the pipettes are removed by means of a small syphon, and the pipettes thoroughly washed out with water, before introducing the fresh reagent. Should any of the absorption liquid have got into the capillary tube above the stopcocks of the pipettes, the tubes must be thoroughly washed out with water through the tap *c*, and the water in the burette and pressure bottle renewed. It is important to grease all the stopcocks carefully before the apparatus is put aside after use.

As the result of the experience of more than four thousand analyses, Fischer regards this form of apparatus as the most suitable for the examination of the gases from boiler furnaces,[1] heating apparatus, brick kilns, pottery kilns, ultramarine kilns, black-ash furnaces,[2] and the like, and also as advantageous for the examination of blast-furnace gases, cupola-furnace gases,[3] the gases from puddling furnaces,[4] the saturation gases in the manufacture of sugar, and for the study of petroleum lamps and of gas engines.[5]

Lunge's modification[6] **of the Orsat apparatus** (Fig. 150) is arranged for the determination of hydrogen, in addition to that of carbon dioxide, oxygen, and carbon monoxide. The pipettes *b*, *c*, *d*, are provided for the absorption of the latter gases, and are charged with potassium hydroxide, alkaline pyrogallol, and cuprous chloride respectively; the manipulation of the apparatus is in every way similar to that of the Orsat-Fischer form. Hydrogen is determined by combustion over a palladium asbestos fibre, placed in the capillary tube *f*, connected to the pipette *h*, which is filled with water, and through the tap *e*, to the capillary connecting tube of the apparatus. The small spirit-lamp *g*, carried by the movable rod *i*, is for heating the palladium asbestos. To carry out the combustion, the residual gas, after the absorption of the carbon dioxide, oxygen, and carbon monoxide, is first mixed with air in the burette *a*, by lowering the pressure bottle, and admitting through the tap *k* sufficient air to bring the total volume to about 100 c.c. If the gas is very rich in hydrogen, it is advisable either to add a further proportion of air after the first combustion has been completed, or to repeat the combustion with the residual mixture, or to substitute oxygen for air in the first instance. The reading of the total volume of gas and air (or oxygen) is first taken, and the mixture passed through the tap *e*, over the palladium asbestos, previously gently

[1] *Dingl. polyt. J.*, 1878, **229**, 130; 1879, **232**, 346; **233**, 183. *Fischer's Jahresber.*, 1881, **27**, 146, 1045 and 1050; 1882, **28**, 131; 1883, **29**, 1289; 1885, **31**, 1295.

[2] *Fischer's Jahresber.*, 1878, **24**, 431; 1880, **26**, 274; 1881, **27**, 35 and 1047.

[3] *Ibid.*, 1879, **25**, 71; 1884, **30**, 37; 1885, **31**, 37.

[4] *Ibid.*, 1881, **27**, 35.

[5] *Ibid.*, 1883, **29**, 1229.

[6] *Dingl. polyt. J.*, 1882, **245**, 512.

heated; the temperature of the tube should be such as to allow of its being touched, for a moment, without burning the fingers. The progress of the combustion is at once indicated by the glowing of the asbestos thread at the end where the gas enters, and by carefully syphoning the mixture backwards and forwards several times, complete combustion is effected as shown by the volume remaining constant. If any residue of carbon monoxide is oxidised with the hydrogen, the

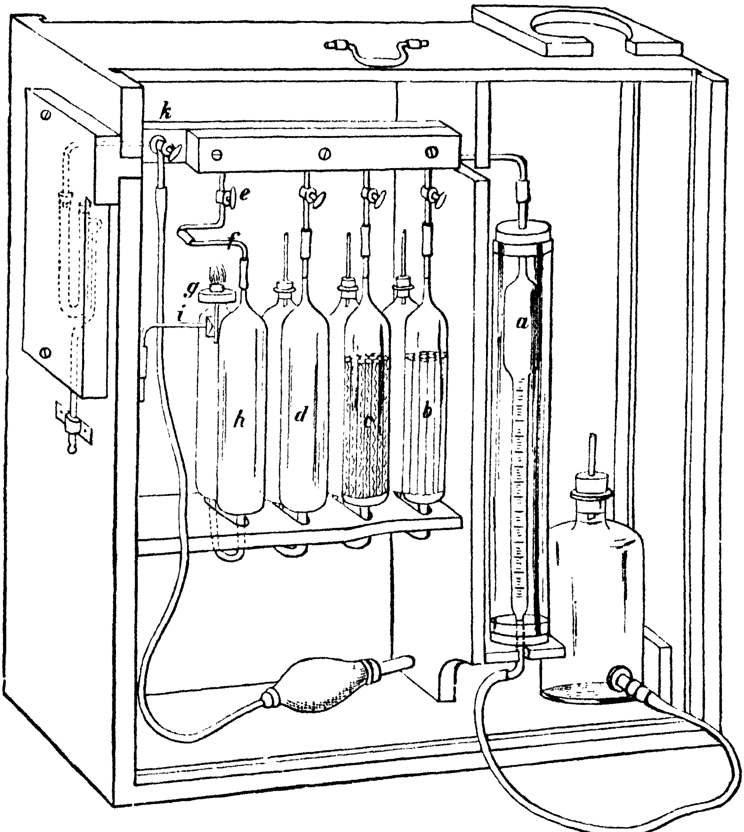

Fig. 150.

residual gas must be passed into the pipette *b*, to remove the carbon dioxide formed, and the total contraction measured after this absorption.

Example of Analysis.

100 *c.c. of Producer Gas gave the following readings on the burette :—*

1. *After absorption of Carbon Dioxide*	3·2
2. *After absorption of Oxygen*	3·2
3. *After absorption of Carbon Monoxide*	24·2
4. *After addition of Air*	0·9
5. *After Combustion*	10·8
6. *After absorption of Carbon Dioxide formed in* 5	11·4

The percentage volumes of carbon dioxide and oxygen are obtained directly from the above data. The total contraction is $11{\cdot}4-0{\cdot}9=10{\cdot}5$; of this $11{\cdot}4-10{\cdot}8=0{\cdot}6$ is due to the formation of carbon dioxide, and since carbon monoxide forms its own volume of carbon dioxide, on combustion, this represents the volume of carbon monoxide present and not previously absorbed by the cuprous chloride solution. The total carbon monoxide is, therefore, $24{\cdot}2-3{\cdot}2+0{\cdot}6=21{\cdot}6$. Since both 2 volumes of hydrogen and 2 volumes of carbon monoxide require 1 volume of oxygen for combustion, two-thirds of the total contraction represents the hydrogen and unabsorbed carbon monoxide, and by subtracting the latter, the volume of hydrogen present is obtained—$(11{\cdot}4-0{\cdot}9\times\frac{2}{3})-0{\cdot}6=6{\cdot}4$. The composition of the gas is therefore:—

Carbon Dioxide	3·2
Oxygen	0·0
Carbon Monoxide	21·6
Hydrogen	6·4
Nitrogen and some Methane	68·8
	100·0

W. H. Sodeau's modification[1] **of the Orsat apparatus** is designed for the analysis of mixtures containing small proportions of combustible gases, and is especially applicable to the examination of chimney gases. It can be readily used in the stokehold, and in combination with a suitable high temperature thermometer it affords a ready means of determining the total chimney losses, including those due to unburnt hydrogen, which are usually ignored; the efficiency of boilers can thus be ascertained. The distinguishing feature from the ordinary Orsat is the replacement of the cuprous chloride pipette and palladium combustion tube, by an adaptation of the Winkler combustion pipette (p. 257). The apparatus is shown in Fig. 151.

The combustion pipette may consist of two separate vessels, the combustion bulb O and the aspirator CR, as shown in the figure, or it may be shaped somewhat like an ordinary Hempel pipette for solid absorbents (Fig. 141, p. 266), provided with a straight instead of with a bent capillary tube. The bulb O is provided with a spiral of platinum wire 0·25 to 0·3 mm. in diameter, attached to a pair of unlacquered brass electrodes, and heated by a current of about 5 amperes, obtained either by means of a 4-volt accumulator, using a short length of iron wire as a controlling resistance, or from a lighting circuit, connected through a few lamps in parallel; water is used as the confining liquid. A lens L, mounted on a fitting which slides on a vertical rod, gives increased accuracy in reading, owing to the elimination of errors of

[1] *Chem. News*, 1904, 89, 61; B. P. 12225, 1906.

parallax. The pipettes K and P are for the determination of carbon dioxide and of oxygen respectively.

Analysis of chimney gas. After determining the carbon dioxide, as usual, by means of the potash pipette K, the gas is passed into the combustion pipette and the current turned on for one to two minutes, when the gas is syphoned back and the contraction measured. The carbon dioxide produced by the combustion is then determined by a one-minute absorption in the pipette K; the decrease in volume gives the percentage of carbon monoxide. Half the volume of the carbon dioxide produced represents the contraction due to the combustion of the carbon monoxide; this value is deducted from the total contraction on combustion, and two-thirds of the difference equals the percentage of hydrogen present. Only one absorbent is thus required for the analysis. The determination of these three constituents can be completed within fifteen minutes, and by means of appropriate curves the results can be stated as lbs. of air used per lb. of fuel, and loss of heat as unburnt gases, provided the composition of the fuel is approximately known. For ordinary practical purposes, the determination of oxygen is, therefore, unnecessary. It may, however, be carried out by means of the pyrogallol (or phosphorus) pipette P, either after the other constituents have been determined, in which case the amount consumed in the combustion is added, or else immediately after the first determination of carbon dioxide, in which case it is necessary to draw in a little air and to re-measure the total volume before combustion.

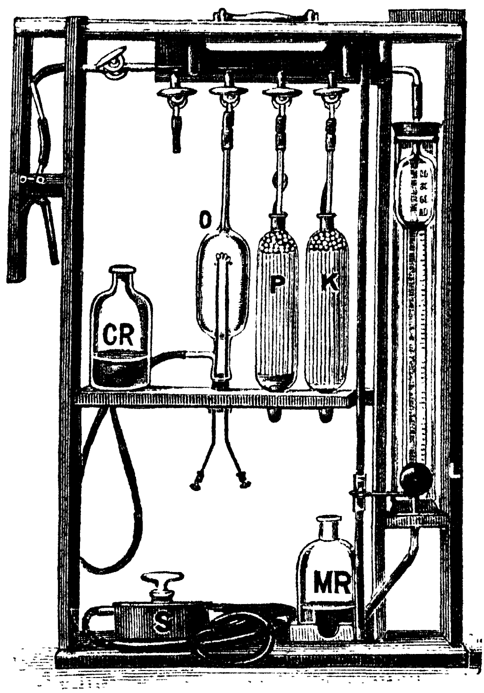

FIG. 151.

Rapid joint estimation of carbon monoxide and hydrogen. As these two gases are, volume for volume, of nearly identical calorific value, it often suffices to make a joint determination of the two, after absorption of the carbon dioxide. For this purpose it is necessary to employ a combustion pipette with a movable reservoir, CR, as shown

in Fig. 151. The measurement after combustion is omitted, in order to save time. The large stopcock S is closed as soon as the gas has been driven over into the combustion pipette O. After combustion, the tap of the potash pipette K is opened, and the gas directly transferred, by raising CR and finally closing the tap of O; after allowing one minute for absorption, the stopcock S is opened, the residue drawn back into the measuring tube, and the tap of K closed. Two-thirds of the contraction equals the percentage of "combustible gases," *i.e.*, carbon monoxide and hydrogen.

A simpler and more compact form of this apparatus is also made which is specially suitable for the work of marine engineers.

A modified Orsat apparatus, specially designed for the analysis of producer gas, has been devised by Meyer.[1] The measuring burette has a capacity of 120 c.c., and a platinum spiral combustion pipette is provided.

Bunte's Gas Burette[2] (Fig. 152) is a development of a simpler form of apparatus due to Raoult,[3] and consists of a burette A provided with taps *a* and *b*, of which *b* is a three-way cock; the burette is fitted with a water-jacket to protect it against rapid changes of temperature. The space between the taps is rather more than 100 c.c., and is divided into fifths of a c.c. The 100 c.c. division coincides with the bottom of the tap *b*, and the zero is 6 or 8 cm. above the lower tap *a*; the divisions are marked for 10 c.c. below the zero. The funnel *c* is provided with a mark, and all measurements are made at atmospheric pressure, plus the pressure of a column of water, contained up to this mark in the funnel. The reservoir C, which can be attached to the bottom of the burette by a rubber tube as shown, serves to fill the burette with water, or an ordinary funnel may be used.

The sample of gas to be analysed is introduced by first filling the burette with water from the reservoir C; the taps *a* and *b* are then closed and the rubber tube from C detached. The three-way tap *b* is then connected with the gas supply, and the sample drawn into the burette by running water out of the bottom tap *a*. Rather more than 100 c.c. of the gas is drawn into the burette, and the adjustment to the zero mark is then made by means of the aspirating bottle S, which serves for forcing water into the burette, or for withdrawing it therefrom. The rubber tube *s* is filled with water by blowing at *t*, so as to remove all air, and whilst the water is still running out, it is attached to the tip of the burette at *a*. For the adjustment, the gas in the burette is compressed to about 95 c.c. by forcing water in from the bottle S. The tap *a* is then closed, *s* detached, and the water cautiously run out, through *a*, exactly to the zero mark. The gas is now under

[1] *Z. angew. Chem.*, 1905, **18**, 446. [2] *Dingl. polyt. J.*, 1878, **228**, 529.
[3] *Comptes rend.*, 1876, **82**, 844.

excess pressure, which is corrected by filling the funnel *c* up to the mark with water, and then momentarily opening the tap *b*, when the excess of gas escapes through the water. The burette now contains exactly 100 c.c. of gas at the atmospheric pressure, plus the pressure of the column in the funnel *c*. When the burette is filled by drawing the sample of gas through it with an aspirator until all the air has been expelled, the adjustment is made by compressing the contained gas, by attaching the vessel C to the burette, and then adjusting as above.

In order to absorb any one of the constituents of the gas, the absorbing liquid is introduced into the burette by first drawing off the water below the zero mark by means of S, the rubber tube *s* being attached to the burette, after first filling it with water. The tap *a* is then opened, and by applying suction at *t*, the water is readily withdrawn to a point a little above the stopcock. The suction bottle is then disconnected, the burette removed from the clamp, and the lower end inserted in a cup containing the absorbent, when on opening *a* the liquid at once rises into the burette. The tap is then closed and the

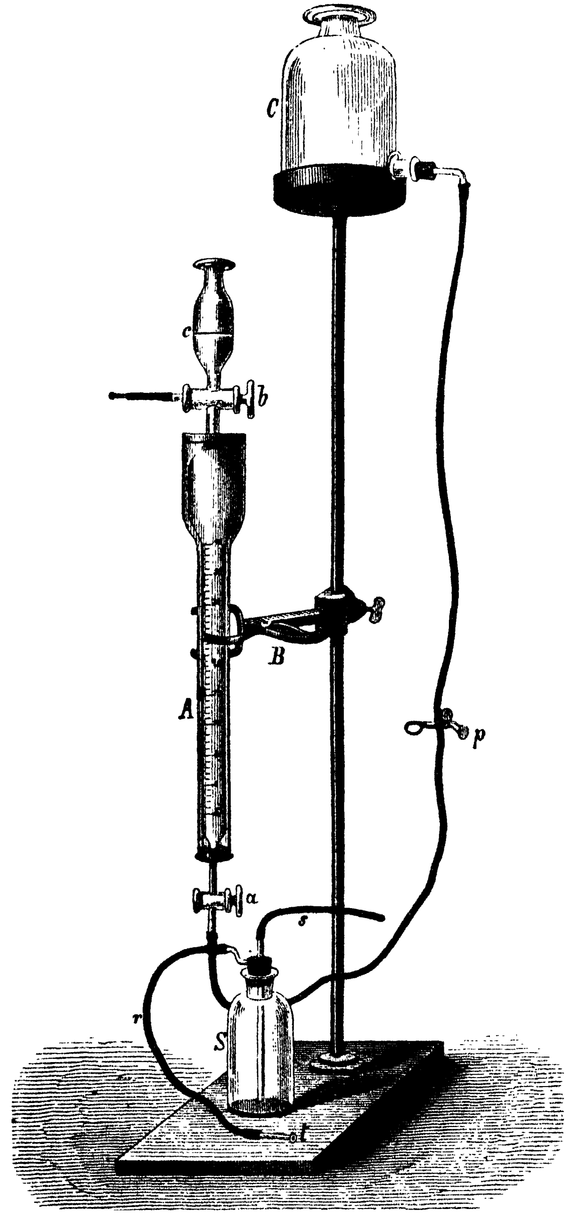

FIG. 152.

contents of the burette well shaken to facilitate the absorption of the gas. A further quantity of liquid is then admitted as before, and this is repeated, the burette being shaken after each absorption, until the level of the liquid in the burette remains constant. The pressure is adjusted by filling the funnel *c* with water and opening the tap *b*, when a little water will enter the burette; the adjustment for pressure is completed by filling *c* to the mark with water and then closing *b*, when the reading can be taken.

As the absorption liquids adhere to the walls of the burette, it is preferable to replace them by water before the final readings are taken, by removing the absorption liquid by means of the suction flask, and replacing it by water, introduced through the funnel *c*; after repeating this two or three times, the liquid is completely replaced by water. Another method is to wash out the burette by a steady stream of water, introduced through the funnel *c*, and run out through *a*, the two taps *a* and *b* being opened during the washing; when the absorption liquid has been fully removed, the pressure is adjusted as before, and the reading taken. Further absorptions are effected successively by suitable absorbents; the composition of the solutions employed is given on pp. 241-247.

After each analysis the burette should be thoroughly cleaned, as otherwise errors are likely to arise, especially in the determination of carbon dioxide, which may be either absorbed or produced by dirt present in the burette.[1]

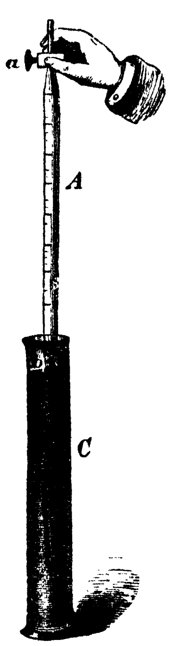

FIG. 153.

Honigmann's Gas Burette.—This burette is especially intended for the estimation of carbon dioxide in the carbonating gases of the ammonia-soda process. It consists of a measuring tube A (Fig. 153), of 100 c.c. capacity, closed at the top by the tap *a*, and open at the bottom, where a stout rubber tube is attached at *b*. The absorbing liquid is contained in the cylinder C. The sample of gas is introduced through *a*, by an aspirator, and after all air in the burette has been thus expelled, the tap is closed and the burette immersed to the zero mark in C, which is filled with a solution of potassium hydroxide; the tap *a* is then opened momentarily, and exactly 100 c.c. of gas, at the atmospheric pressure, is obtained. The absorption is effected by first immersing the burette somewhat lower in the solution, so as to wet the sides with the absorbent, and then drawing it out, so that the bottom of the rubber tube remains in the solution, whilst the burette

[1] *Cf.* F. Fischer, *Z. angew. Chem.*, 1890, 3, 599; Haldane, *Methods of Air Analysis*, 1918, pp. 39-42.

is raised over the edge of the cylinder. The potassium hydroxide at once begins to enter the burette, and after agitating a few times the absorption is rapidly completed. The burette is then placed in the liquid, so that the inner and outer levels are the same, and the reading taken. The method is not one of great accuracy, but it is extremely simple and quick.

Pfeiffer's Gas-Analysis Apparatus.[1]—The following considerations have been advanced by Pfeiffer with regard to the method of analysis adopted, more especially with his apparatus. The errors that may arise in the estimation of carbon monoxide by absorption with cuprous chloride are not altogether overcome by using a second absorption pipette, as a partial absorption of the residual gases, other than carbon monoxide, may possibly occur. Pfeiffer therefore considers that it is both simpler and more accurate to estimate the carbon monoxide by explosion simultaneously with the hydrogen and methane. He also prefers to oxidise the hydrogen and methane together, rather than to adopt the method of fractional combustion. From these considerations the course of analysis adopted consists in the successive estimation of the carbon dioxide, heavy hydrocarbons, oxygen, and possibly the hydrocarbon vapours by absorption, and the combustion of the residual carbon monoxide, hydrogen, and methane. By estimating the carbon dioxide formed, the total contraction, and the residual nitrogen, after the removal of the excess of oxygen by means of phosphorus, the necessary data for calculation on the lines described on p. 258 are obtained. A complete analysis of coal gas can be carried out by this method in three-quarters of an hour, and very accurate results, it is stated, can be obtained.

The apparatus consists of the burette and levelling bottle (Fig. 154), two or three absorption pipettes (Fig. 155), a phosphorus pipette, and an explosion pipette (Fig. 132, p. 254).

The burette B, which serves as the measuring tube, is provided with a stopcock *b*, and funnel, and is attached to the pipette P, as shown; the capacity of the burette is 100 c.c. The lower end of the burette is connected by the rubber tubing S, with the levelling bottle N, of 300 c.c. capacity. Water acidified with 0·5 per cent. of sulphuric acid is used as the confining liquid to prevent the absorption of carbon dioxide and to take up ammonia vapour after the absorption of the hydrocarbon vapours.

The absorption pipette, which permits of the replacement of the gas in the capillary connecting tube by water, is shown in Fig. 155, the capillary side tube *c* being connected to the burette; by altering the position of the stopcock *p*, in a manner which can be readily seen from the diagram, water may be run from the funnel *t* into the capillary

[1] *J. Gasbeleucht.*, 1899, 42, 209.

c, and the air expelled before connecting with the burette; and when drawing the gas back to the burette after absorption, the absorbing liquid is allowed to rise only to the stopcock *p*, after which, by turning the latter through an angle of 90°, water is run from the funnel *t* into the capillary *c*, thus forcing the gas which remains in it into the burette; this operation is carried out before each reading. In place of the wooden or metal stand used by Hempel, the tube is bedded in a sheet metal case by means of paraffin wax or plaster of Paris.

The burette B is first filled completely with water by raising the

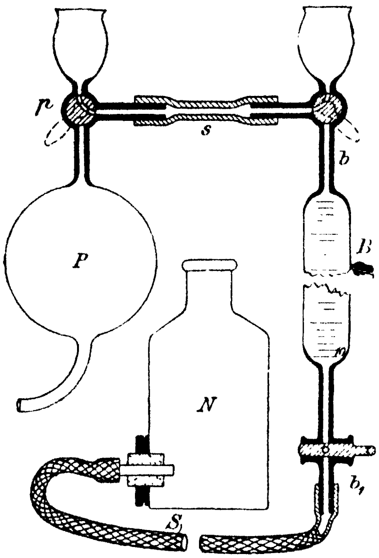

FIG. 154.

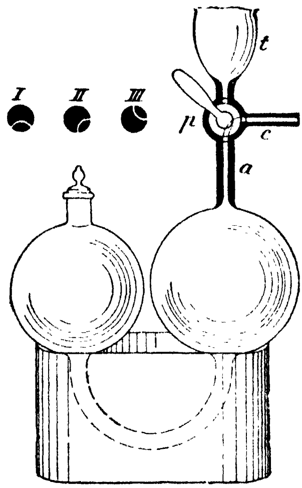

FIG. 155.

levelling vessel and opening the stopcocks *b* and b_1 and the sample then drawn in by lowering the levelling bottle in the usual manner, until the volume of gas is a little below the zero mark; the stopcocks are then closed, and the levelling bottle again raised. To measure off exactly 100 c.c., the lower stopcock is carefully opened and the water allowed to rise to the true zero; the upper stopcock is then momentarily opened, and the volume checked in the usual manner with the levelling bottle N. In the first reading the zero lies as much below the zero mark as is equivalent to the content of the capillary at *b*, since the latter is filled with water in the subsequent measurements and the 100 c.c. graduation is at the lower end of the capillary. This correction (generally 0·2 c.c.) is, therefore, determined once for all as follows:—Air is introduced into the burette to about the division 90, then water until the capillary at *b* is filled, the stopcocks closed, and the reading taken after two minutes; meanwhile the water is completely removed from the capillary tube of the stopcock, the water then run out of the

capillary into the burette and another reading taken; the difference between the two readings gives the capacity of the capillary. It is advantageous to use a meniscus screen, such as that of Göckel (p. 36), in taking the readings.

An improved form of burette designed by Pfeiffer,[1] especially for the analysis of coal gas, is shown in Fig. 156, and as arranged for the explosion of the combustible gases in Fig. 157. The bulb at the top of the burette is connected by a narrow tube to the lower bulb, which latter is provided with a mark *m*, which serves for measuring off the gas residue taken for combustion. The total capacity of the burette between the two stopcocks is sufficient to contain the volume of air requisite for the combustion of the above gas residue. The relative capacities of the two spaces, for coal gas and for carburetted water gas, should be about 1:5. The capacity of the burette to *m* is marked (R), also the total capacity (J), and the volume of nitrogen contained in J when filled with air, N_1.

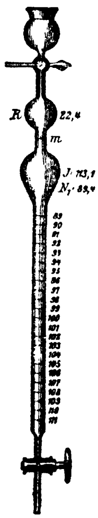

FIG. 156.

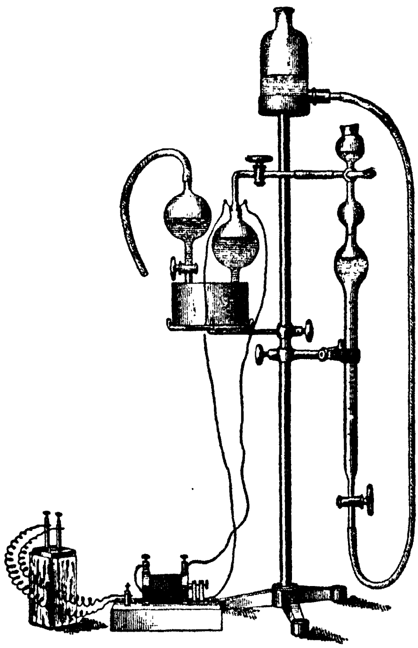
FIG. 157.

Carbon Dioxide. The pipette (Fig. 155, p. 282) is filled up to the tap with potassium hydroxide, and is connected with the burette as shown in Fig. 154. The stopcocks of both the burette and pipette are turned to the position in which the two funnels communicate with each other, water poured into one of them to expel the air from the connection *b-s-p*, the stopcocks of the pipette and of the burette turned through 180°, and the gas transferred from the burette into the pipette. While it is passing over, the contents of the pipette are shaken for a moment, so as to mix the water from the capillary connections with the alkali. As soon as the water reaches the stopcock *p*, the burette stopcock *b* is closed; the absorption is complete in one minute. The gas is then syphoned back to the burette by lowering the levelling bottle until

[1] *Z. angew. Chem.*, 1907, **20**, 22.

the alkali reaches the stopcock *p* of the pipette, which is then turned through 180°, and the gas in the capillary, *p-s-b*, washed out as before by means of the water in the pipette funnel. The burette stopcock *b* is then closed and the reading taken as usual, after allowing to stand for one minute.

Benzene Vapour.—This is absorbed with ammoniacal nickel cyanide solution (p. 242); after shaking for three minutes (it is preferable to facilitate the shaking in this case by detaching the pipette), the residual gas is returned again to the burette where the absorption of the ammonia vapours is effected by the acidulated water used as the confining liquid. As a check, about 0·5 c.c. of fresh acidulated water is introduced into the burette from the pipette funnel.

Total Heavy Hydrocarbons, or only ethylene if benzene is previously absorbed, are determined by absorption with bromine water, and the bromine vapours subsequently removed by potassium hydroxide; three minutes, with frequent shaking, is necessary for the absorption.

Oxygen is estimated in the phosphorus pipette. The capillary space between the pipette and burette is cleared by forcing the water from the pipette into the burette funnel by attaching a piece of rubber tubing to the open end of the pipette and blowing.

Carbon Monoxide, Hydrogen, Methane, and Nitrogen. The explosion pipette (Fig. 132, p. 254, and Fig. 157, p. 283) is used for the estimation of these gases. In the analysis of coal gas, from 20 to 22 c.c. of the gas left after absorption, which requires about five volumes of air for combustion, is first measured off in the burette by allowing the excess to escape; since, in doing so, the capillary at *b* is freed from water, its capacity, as determined, must be added to the reading. The burette and explosion pipette are then connected, the air in the connecting capillaries displaced as described above, and the gas passed over. The explosion pipette is then disconnected and the burette filled with air. The air is then transferred to the explosion pipette, the water allowed to rise as far as the bulb of the pipette, the stopcock *a* is closed, and the small quantity of water remaining in the explosion chamber A withdrawn into the reservoir B, so that only the V-shaped connection remains filled with water; the stopcock *b* is then closed. The mixture is sparked in the usual manner, the pipette stopcock carefully opened so that the enclosed water comes back into the explosion chamber slowly, and the residual gas, consisting of nitrogen, carbon dioxide, and a little oxygen, passed back into the burette.

The carbon dioxide formed in the combustion is then absorbed with potassium hydroxide, and the excess of oxygen with phosphorus, whereby a direct measurement of the total nitrogen, inclusive of that added as air, is obtained.

Bone and Wheeler's Apparatus.—This apparatus,[1] which is exceedingly convenient for the rapid analysis of all gases met with in gasworks, is a simplified form of the apparatus employed by Bone

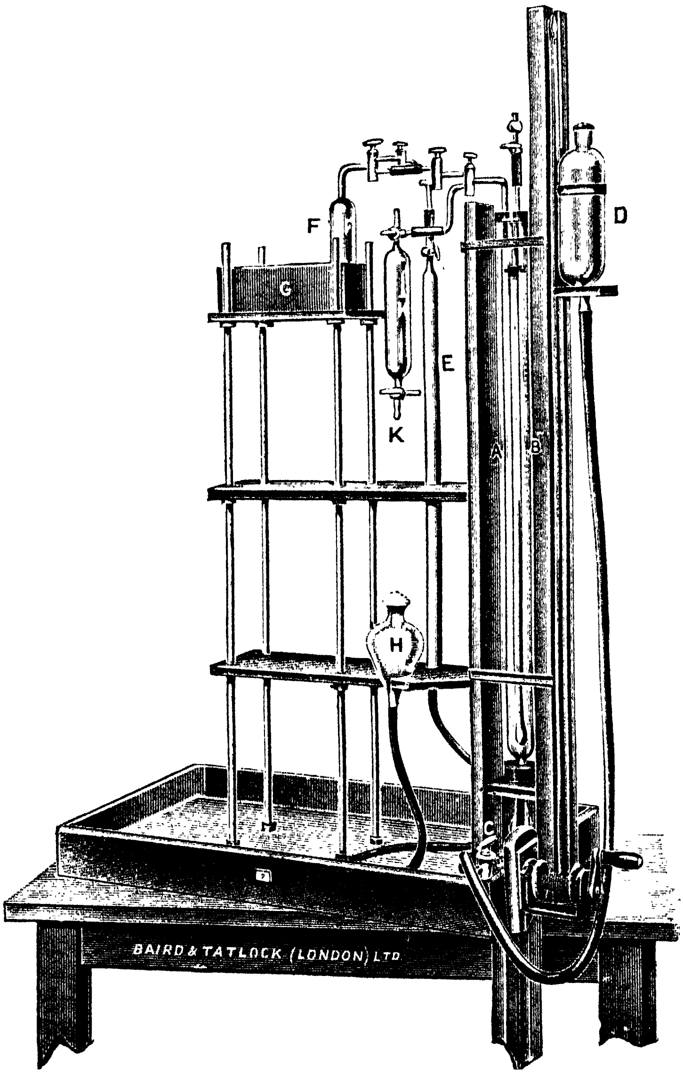

FIG. 158.

for research,[2] which was in turn a modification of the Frankland apparatus, including alterations introduced by Macleod and Dixon.

The arrangement of the various parts of the apparatus is shown in Fig. 158. It comprises, essentially, three parts, viz.:—(1) a water-

[1] *J. Soc. Chem. Ind.*, 1908, 27, 10.

[2] *Proc. Chem. Soc.*, 1898, p. 154.

jacketed combination of measuring and pressure tubes, A and B, communicating, through the glass tap, C, with the mercury reservoir, D; (2) an absorption vessel, F, standing over mercury in a porcelain trough, G; (3) an explosion tube, E, fitted with firing wires, and connected with a separate mercury reservoir, H. All the connections between A, E, and F are of capillary bore, with suitable glass taps where necessary. The diagram also shows how connection is made between the measuring tube, A, and the special "sampling tube," K, when the latter is employed for the introduction of the sample under examination. The sample may also be introduced into the apparatus from an ordinary test tube inserted under the wide, open end of the absorption vessel, F, filled with mercury. Before commencing an analysis, the whole of the apparatus, including all the connections between A, E, and F, is completely filled with mercury, and all the subsequent operations are conducted over mercury.

The various parts of the apparatus are suitably mounted on a strong wooden stand (oak or teak), with four vertical steel rods supporting the shelf upon which the mercury trough, G, rests; the same rods also carry another shelf for reagent bottles. The mercury reservoir, D, can be raised or lowered (to the ground level, if required) by means of a wooden carrier with suitable pulley and ratchet wheel. The whole apparatus stands in a wooden tray 2 ft. 4 in. by 1 ft. 6 in. with 1 in. raised sides.

The salient features of the working of the apparatus are as follows:—

(1) The principle of measurement is that first introduced into gas analysis by Regnault, and subsequently adopted by Frankland, viz., the measurement of the pressure of the gas (in mm. of mercury) at constant volume. For this purpose the gas is brought to a certain "constant volume" mark in the measuring tube, A (by suitable manipulation of the mercury reservoir D and the tap C), and its pressure read off on the pressure tube, B. There are a series of such "constant volume" marks on A, each coinciding with a 100 mm. mark on the pressure tube, B (*i.e.*, with 0, 100, 200, etc., mm.), so that the actual pressure of the gas is given by subtracting from the "pressure reading" the numbers 0, 100, or 200, etc., according to the particular constant volume mark selected for the analysis. The tubes A and B are made in one piece, and are surrounded by a water-jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube with alkalis; the wetting of A and B with the same liquid eliminates the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The

tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing, a device which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in B is inadvertently allowed to run up the tube with unusual velocity. This tap also allows of a vacuum being easily made in B whenever necessary. The advantages of this mode of measurement over the more usual method of determining the volume under atmospheric pressure are twofold, viz., (*a*) it allows of the use of smaller volumes of gas for an analysis; thus from 5 to 10 c.c. of gas can be made to have a pressure of 100 mm., according to the particular volume mark selected, and this pressure can easily be read off to within 0·2 mm. without employing a telescope; and (*b*) the measurements are, of course, independent of readings of the barometric pressure, and at the same time are unaffected by the tension of aqueous vapour.

(2) The length of the pressure tube, B (about 700 mm.), amply provides for the proper dilution of the "explosive mixture" in an explosion analysis, even in the case of a rich gas such as coal gas.

(3) The arrangements for the various "absorptions" are simple, all being carried out over mercury in the one absorption vessel, F, with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use.

To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid *in situ* between each successive reagent, the wide (open) end of the vessel is immersed under the mercury in the trough, G, whilst the top terminates in a capillary three-way tap. One of the parallel branches of this tap communicates through a stout rubber joint, with the measuring vessel, A, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel to serve as a trap for either the mercury or the reagent which is being discarded after use. The insertion of a tap between the pump and the bottle obviates the necessity of the continuous exhaustion of the latter, a single exhaustion at the outset of an analysis being all that is required.

From 2 to 5 c.c. of the reagent to be used is introduced into the absorption vessel (previously filled with mercury), by means of a suitable pipette, from below the surface of the mercury in the trough. Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the tap leading to the above-mentioned exhausted bottle; the same device allows of the complete withdrawal of the reagent after use, without taking down the absorption vessel, and also of the rinsing out of the latter *in situ* with water, or dilute sulphuric acid, before the next reagent is used.

The apparatus is arranged for fixing at the right-hand end of the laboratory bench, the guide rail for the mercury reservoir D being extended to the ground level. A water supply and suitable waste pipe are required for the circulation of water through the water-jacket surrounding the measuring and pressure tubes, and a filter pump for evacuating the large bottle used as a trap for the waste reagents and for any mercury carried over with them.

As the gas during the analysis is for the most part under considerably less than atmospheric pressure, it is essential for accuracy that the stopcocks should be perfectly tight; provided that care is exercised in their selection, and that they are carefully lubricated, no difficulty is experienced in this respect. A suitable lubricant is prepared as described on p. 235. In cleaning the stopcocks a soft linen rag should be used, to avoid any abrasion of the ground surfaces. After each analysis the apparatus should be washed out with 5 per cent. sulphuric acid.

In the analysis of illuminating gas, the sequence of operations is similar to that adopted with other forms of apparatus. The carbon dioxide is best absorbed with 25 per cent. potassium hydroxide solution, and the heavy hydrocarbons with a solution of bromine in aqueous potassium bromide, followed by potassium hydroxide. For the absorption of oxygen, 5 to 8 c.c. of very concentrated potassium hydroxide solution is first placed in the absorption vessel, and then 2 c.c. of pyrogallol solution (1 oz. in 100 c.c.). For the carbon monoxide, two absorptions with 8 to 10 c.c. of the solution of ammoniacal cuprous chloride, made up as described on p. 243, are made, and the gas washed with 5 per cent. sulphuric acid.

The whole of the residue is then mixed with at least twice its own volume of excess oxygen[1] or air (the quantity of gas originally taken must allow of this being done). The gas is transferred to the explosion tube, fired in the usual manner under reduced pressure, then drawn back into the measuring vessel, and the contraction determined. The carbon dioxide formed by the explosion of the methane is then determined by absorption with potassium hydroxide.

The following table shows the method of recording the results in an analysis of coal gas:—

V = Constant volume mark selected on measuring tube.
R = Reading of barometer tube when gas is brought to the constant volume mark selected. Hence, $R - V$ = pressure of gas.
T = Temperature of water-jacket.
C = Contraction on explosion.
A = Absorption by potassium hydroxide after explosion.

[1] Conveniently prepared by the interaction of a solution of hydrogen peroxide and a 5 per cent. solution of potassium permanganate.

	Constant Mark, V.	T.	R.	Difference.	Remarks.
Original gas . .	0	15°·2	168·0	...	Gas taken = 168·0.
After KOH . .	0	15°·2	164·0	4·0	$CO_2 = 4·0 \times 100 \div 168·0$ = 2·4 per cent.
„ Br . .	0	15°·2	158·1	5·9	$C_nH_m = 5·9 \times 100 \div 168·0$ = 3·5 per cent.
„ Pyrogallol .	0	15°·2	157·6	0·5	$O = 0·5 \times 100 \div 168·0$ = 0·3 per cent.
„ Cu_2Cl_2 . .	0	15°·2	143·3	14·3	$CO = 14·3 \times 100 \div 168·0$ = 8·5 per cent.
Oxygen added . .	0	15°·2	588·1	...	$CH_4 = 52·9 \times 100 \div 168·0$ = 31·5 per cent.
After explosion .	0	15°·2	359·5	228·6C	$H = \frac{2}{3}(228·6 - 2 \times 52·9) \times 100$
„ KOH . .	0	15°·2	306·6	52·9A	$\div 168·0 = 48·7$ per cent.

Therefore:—

CO_2 = 2.4 per cent. CO = 8.5 per cent.
C_nH_m = 3.5 „ CH_4 = 31.5 „
O_2 = 0.3 „ H_2 = 48.7 „
N_2 (by difference) = 5.1 per cent.

Haldane's Apparatus.—Haldane[1] has devised two forms of apparatus[2] which have found wide application, more especially for the analysis of mine air.

The larger form of apparatus, which gives the more accurate results, is shown in Fig. 159. When mine or other air is being investigated, the sample is collected in a 3-oz. bottle (about 90 c.c.). The stopper is greased with vaseline, and during transport is held firmly in position by an elastic band. The bottles must be dry and clean. They should be cleaned with a brush, rinsed with clean (preferably distilled) water and dried completely. (Alcohol, ether, etc., should not be used for this purpose, as traces may cause serious error.)

To introduce the sample of gas into the apparatus, the bottle is inverted in a mercury trough and the stopper removed, under the surface of the mercury, by means of a pair of crucible tongs. The sample is then drawn in through a curved tube attached at C. The gas-burette A is about 32 in. (800 mm.) long, and is provided at the top with a three-way tap. Its upper wide part is about 25 mm. in diameter and has a capacity of about 15 c.c. The graduation, which is to 0.01 c.c., extends down the narrow part, which is 3.5 mm. in bore, from about 15 to 21 c.c., the capacity being measured from the tap (not including its bore) to the upper surface of the mercury. There are

[1] See *Journal of Physiology*, 1898, **22**, 466.

[2] These are supplied by Messrs Siebe, Gorman & Co., 187 Westminster Bridge Road, London.

also marks at the initial 5 c.c. on the wide part. With this burette it is possible to read the gas volume without the aid of a telescope, correct to 0·001 c.c. A water-jacket surrounds the gas-burette, and the water is mixed by blowing air through a glass tube passing to the bottom. The burette is connected by means of thick-walled rubber tubing of about 3 mm. bore, with the levelling tube B about 15 mm. wide, and by raising or lowering this tube, gas is expelled from or drawn into the burette, and the pressure of the gas adjusted.

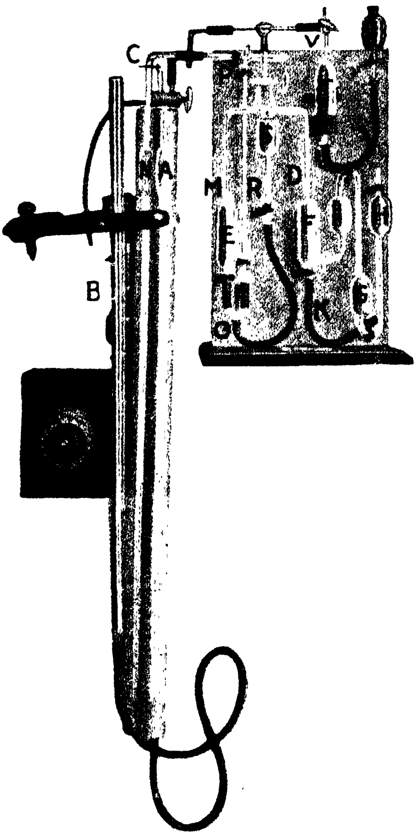

Fig. 159.

One of the three-way connections, C, of the tap on the burette is used for taking in the sample, and the other connects with absorption and combustion pipettes arranged as shown. The absorption pipettes E and F are about 100 mm. by 30 mm., and F is filled with glass tubes to increase the absorbing surface. The glass tubes which lead from them must have a bore of about 2 mm. E is filled with caustic potash or caustic soda solution (about 10 per cent. strength usually, unless gases such as nitrous oxide, which are very soluble in water, are present, when a concentrated solution is employed) and is connected with the movable reservoir S by black rubber tubing. F contains alkaline pyrogallate solution. G and H, each of about 30 c.c. capacity, are partly filled with the strong potash solution, to protect the pyrogallate solution from oxidation and to prevent it from becoming gradually diluted with water.

The pressure in the burette is adjusted by using the potash pipette as a pressure gauge and bringing the surface of the potash before every reading of the burette exactly to the mark M. The control tube N, standing beside the burette in the water-jacket, is employed to make the readings of gas volumes entirely independent of changes of temperature, barometric pressure, and percentage of moisture during the analysis. The connecting tubes from N are of the same diameter and about the same length as those from the burette. A three-way

tap at P enables N to be connected with the atmosphere. By means of the T-tube O the potash solution is brought into connection with N. At the commencement of the analysis, the potash solution is adjusted to the mark R by raising or lowering the potash reservoir S, P being meanwhile open to the air. P is now turned so that the control tube is connected with the potash tube only, and is not again opened till the analysis is complete. Each time a reading of the burette is made, the potash is brought to the mark R by raising or lowering S. The potash in the absorption pipette is then brought to the corresponding mark M by adjusting the levelling tube. Readings of the burette are thus compensated for variations of temperature and barometric pressure, which are thus always adjusted to those initially ruling in N. The lower part of the control tube is kept full of water, and the inner surface of the burette is kept moist, so that gas in the burette and control tube is always saturated with water vapour. The water used for moistening the inside of the burette should be slightly acidified with sulphuric acid in case alkali derived from the glass should render it alkaline. If the burette is allowed to become dry, appreciable errors occur.

The combustion pipette T, which is filled with mercury, is about 80 mm. by 30 mm., and contains a spiral of three turns of fine platinum wire which can be heated by current from a four-volt battery, a rheostat being also included in the circuit. The pipette is closed below by a cork soaked in paraffin, so that the platinum spiral may easily be removed when necessary. The cork is secured by wiring to prevent it being driven out by an accidental explosion in the pipette.

In general, at the commencement of an analysis, it is necessary to fill the capillary connecting tubes with nitrogen, *e.g.*, that left at the end of a previous analysis. The pyrogallate, mercury, and potash solution are successively adjusted to the marks D, V, R, and M. The control tube tap is then closed to the atmosphere. The excess of nitrogen in A is expelled through C and the gas to be analysed measured off in A. Carbon dioxide is absorbed first. As the mercury cannot be allowed to pass beyond the tap on the burette, the sample must be passed backwards and forwards two or three times to clear any carbon dioxide from the connecting tube.

When the sample contains only traces of combustible gases, the combustion is effected in T without dilution of the sample. The contraction on combustion is noted and the carbon dioxide formed is absorbed in the usual manner. Residual oxygen is absorbed in the pyrogallate pipette F. If the oxygen content of the sample is to be determined, a separate analysis, omitting the combustion, is performed, and the oxygen consumed in the combustion determined by difference. Methane, hydrogen, and carbon monoxide are determined by calculation from the results as already explained (p. 248 *et seq.*). In many

samples of mine air, methane is the only combustible constituent present; the analysis is then considerably simplified, as the oxygen used in the combustion may be calculated and added to the residual oxygen found by absorption.

When the sample contains much methane or other combustible constituent, it must be diluted with air before combustion. In such case, nitrogen present from the previous analysis should be passed into the explosion pipette. A sample of gas is taken and a preliminary determination of the carbon dioxide and oxygen present made, so

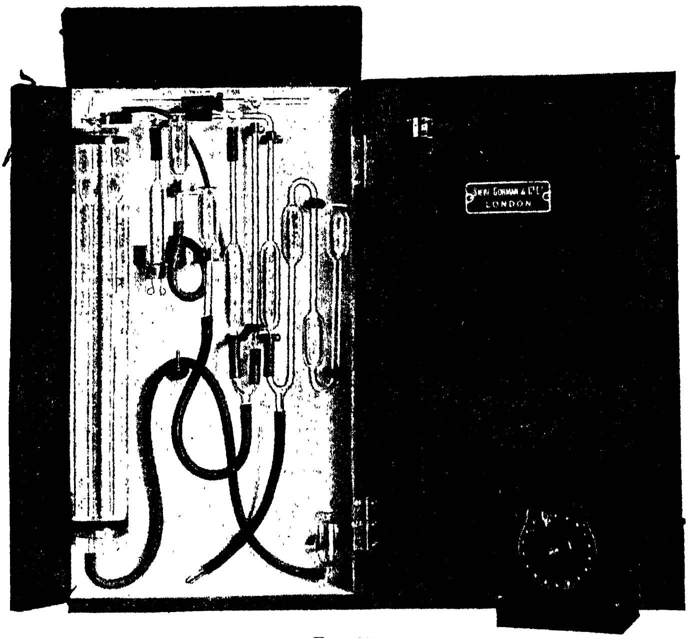

FIG. 160.

that the methane present may be approximately estimated. A mixture of air and gas is then made so that not more than 6 per cent. of methane is present in the mixture. At least 15 c.c. of one constituent must be taken in order to permit accurate measurement. Before the air and gas are measured, the residual gas from the preliminary analysis is swept from the apparatus by means of air, after which the connecting tubes are cleared of air by means of the nitrogen stored in the combustion pipette. The necessary air is drawn into the pipette, deprived of carbon dioxide and measured; this is stored in the potash pipette whilst the gas is drawn into the burette and approximately measured. (Before this is done, air must be expelled from the tube C by means of mercury from A.) The air is returned to the burette and the mixture measured; the accurate

volume of gas taken is determined by difference. The analysis then proceeds as usual.

The apparatus although primarily designed for the analysis of mine air is capable of general application where any particular gaseous constituent in a mixture, diluted with air or other gas, has to be determined with an accuracy of from 0·005 to 0·01 per cent.

A smaller and easily portable form of Haldane's apparatus is shown in Fig. 160. The apparatus is contained in a wooden case of internal dimensions $20 \times 12 \times 2\frac{1}{2}$ in., which can easily be shut up and transported. It is well to cork the open tops of the mercury and potash reservoirs during transportation, in case the apparatus falls over or is laid on its side. The principle adopted and the method of use are exactly the same as in the larger apparatus.

In a further simplified form of the apparatus intended for the determination of small quantities of carbon dioxide only, the combustion and pyrogallate pipettes are eliminated. The manipulation is substantially as described above. Further details will be found in Haldane's *Methods of Air Analysis*, 1918, pp. 67-76, where a number of other modifications of the original apparatus are also described.

Jaeger's Apparatus.—The method of analysis adopted by Jaeger[1] consists in the estimation of carbon dioxide, heavy hydrocarbons, and carbon monoxide by absorption, followed by the fractional combustion of hydrogen and methane over copper oxide at different temperatures; as no air is added for the combustion, the whole of the residual gas after the absorptions can be used for the estimation of these constituents. A further advantage of the method is that the nitrogen can be determined directly.

The apparatus is shown in Fig. 161. The burette is a modified form of that of Bunte, narrowed at the top to permit of more accurate readings and provided with a side exit tube; it is enclosed in a water-jacket. The absorptions are carried out with pipettes in the usual way. For the fractional combustion of the hydrogen and methane, the copper oxide tube (Fig. 136, p. 260) is connected up with short pieces of rubber tubing, s_1, s_2, bound with wire, to a Hempel pipette filled with potassium hydroxide solution on the one side, and with the side tube of the burette on the other. Below the combustion tube is placed the Bunsen burner b, provided with a special regulating tap and a fan-shaped top. A framework of sheet iron attached to the burner carries a cover in which a short thermometer graduated up to 270° is fixed so that its bulb lies close to the side of the combustion tube. At the beginning of the test the solution in the pipette is forced up to the mark m of the capillary by blowing through the tube s_3 when the upper burette cock is in position I.; the stopcock is then closed

[1] *J. Gasbeleucht.*, 1898, **41**, 264; *Z. angew. Chem.*, 1899, **12**, 173.

with a quarter turn (position III.), and the tube slowly heated to 250° and kept at this temperature with as little variation as possible. As soon as this temperature is reached the upper stopcock of the burette is opened (position II.), then the lower one, and the levelling bottle raised. On passing the gas slowly from the burette to the pipette and back again, the hydrogen is completely oxidised. After cooling, the water in the pipette is again brought to the mark *m* and the residual gas measured.

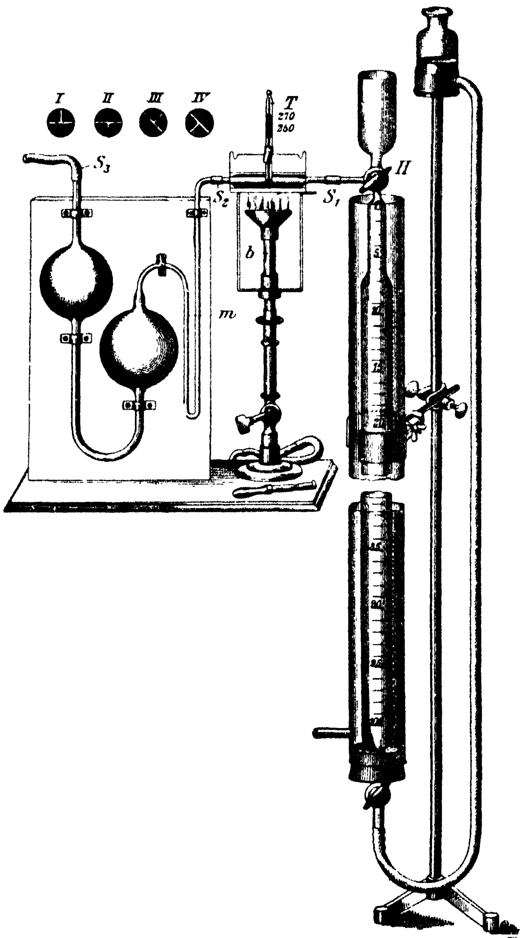

FIG. 161.

The correction to be applied for the oxygen of the air initially enclosed in the combustion tube, which participates in the oxidation of the hydrogen, is made once for all by filling the burette with pure hydrogen and determining the value of the correction; it is approximately 0·5 c.c. and is to be subtracted from the hydrogen contraction found. The correction must also be added to the volume found for nitrogen at the end of the analysis.

For the subsequent combustion of the methane, the cover with thermometer is removed, the tube heated with a more powerful flame to a bright red heat, and the gas repeatedly passed over the copper oxide till no further decrease in volume takes place. The carbon dioxide formed by the combustion is retained in the alkali pipette; the decrease in volume, therefore, corresponds directly (without correction) to the methane present. The residual gas must be allowed to cool to the temperature of the room before taking the final reading.

The incombustible gas residue, increased by the volume of the oxygen previously enclosed in the copper oxide tube and afterwards consumed (correction value), gives the nitrogen content of the gas.

For the determination of the percentage of nitrogen only in a sample of gas, the latter is placed in the burette, the copper oxide tube at once heated to a high temperature, and the gas passed backwards and forwards into the potash pipette until no further contraction occurs. All gaseous constituents other than nitrogen are thus completely removed, and the residual volume of gas, read after complete

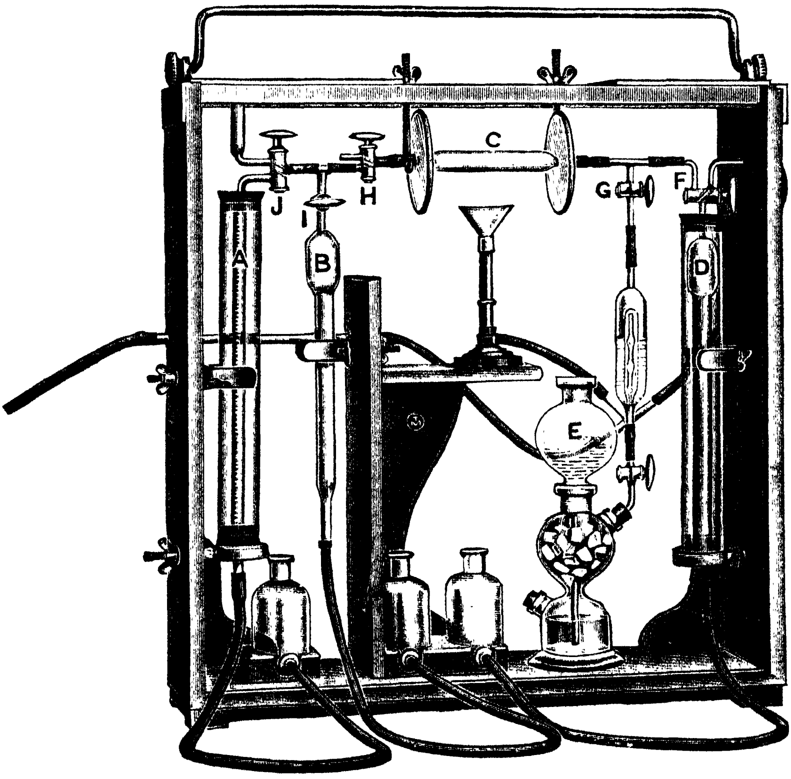

FIG. 162.

cooling, plus the correction for the oxygen content of the copper oxide tube, gives directly the amount of nitrogen in the gas, and its percentage if 100 c.c. have been taken. When many such tests have to be made, it is convenient to displace the air in the copper oxide tube by nitrogen previous to the test; then no correction is necessary.

After each test the copper oxide tube must be heated in a current of air to re-oxidise the reduced copper.

The results obtained by this method are satisfactory as regards accuracy. The combustion of the methane is, however, very slow, and varies greatly according to the physical condition of the oxide of copper.

The "Metrogas" Apparatus.—E. V. Evans[1] has described a form

[1] *Gas World*, 1911, **55**, 814; *J. Gas Lighting*, 1911, **116**, 819.

of apparatus enabling the method of combustion with cupric oxide to be applied very conveniently to the determination of the nitrogen in a gaseous mixture, more especially in illuminating gas.

The apparatus,[1] Fig. 162, consists essentially of a graduated burette A containing sodium hydroxide solution, an acid burette B containing acidulated water, a quartz tube C containing copper oxide, a sampling burette D containing acidulated water, and a CO_2 generating apparatus E.

The apparatus having been proved gas-tight, all air is expelled from the quartz tube and capillary connections by carbon dioxide. The sample of gas is drawn into the burette D and measured at a determined temperature; it is then passed slowly through the tube C heated to redness, into the burette B. The gas is passed backwards and forwards in this manner between B and D several times, after which the residual gas is completely swept into B by means of carbon dioxide. The stopcock H is closed and the mixture of carbon dioxide and nitrogen is transferred to A to absorb the carbon dioxide and measure the nitrogen. If necessary, correction is made for the difference between the temperature of the nitrogen in A and the original temperature of the gas when measured in D.

Balcon[2] and Smith[3] have described modifications of the Bone and Wheeler apparatus (see p. 285 *et seq.*), whereby nitrogen may be directly determined in a somewhat similar manner.

3. Special Methods of Determining Certain Constituents in Gaseous Mixtures, more especially in Crude and Purified Illuminating Gas.

Some of the constituent gases and vapours present in certain gaseous mixtures, *e.g.* in illuminating gas, cannot be readily determined by the methods of volumetric gas analysis already described. For some constituents, such as ethylene, there is no specific absorbent apart from those for other heavy hydrocarbons; the quantity of some others, such as naphthalene and carbon bisulphide, is too small to be determined by the diminution in volume on direct absorption. In such cases, special gravimetric, volumetric, or colorimetric methods are employed.

Examples of titration methods are described for the estimation of sulphur dioxide on pp. 393-400, of hydrochloric acid on pp. 514-516, and of chlorine on pp. 586-598, etc., in the Sections devoted to the industries in which they are mostly employed.

In making tests with crude gas, certain precautions must be taken

[1] Made by Messrs Townson and Mercer, Camomile Street, E.C.3.

[2] *J. Gas Lighting*, 1913, 121, 102.

[3] *Gas World*, 1919, 71, 342.

if results of any reasonable degree of accuracy are to be obtained. The interior surface of the mains of the manufacturing plant is usually coated with tar and ammoniacal liquor or water, and if gas be taken for such tests from a cock on the main, or from a small service pipe leading from the main, the slow stream of gas employed in making the test is largely drawn from that travelling along the surface of the main, which, by the action of the tar and liquor on that surface, is often materially altered in composition as compared with the bulk of the gas passing through the main at that point, with the result that incorrect and often very misleading results are obtained. The most satisfactory plan is to place a cork carrying a piece of glass tubing into a suitable hole bored in the main and closed by a plug when not in use, the end of the glass tube projecting well into the main. The other end of this tube is coupled, with connections as short as possible, to the absorbing apparatus, rubber connections being avoided as far as practicable, and where connections have to be made with such tubing, the ends of the glass tubes joined should be brought close together within the rubber tube, so as to expose a minimum of rubber surface to the gas.

Where a direct connection to the main cannot be made in this manner, and a service pipe leading from it must be utilised, arrangements must be made to ensure the passing of a rapid stream of gas through the latter whilst the test is in progress, the gas actually used in this test being taken off from this service by means of a suitable T-piece. These precautions are also advisable even when testing purified gas, although the error caused by their non-observance is usually not so great.

Special methods of determination are described for ethylene, benzene vapour, acetylene, oxygen, carbon dioxide, carbon monoxide, sulphuretted hydrogen, carbon bisulphide, total sulphur compounds other than sulphuretted hydrogen in coal gas, ammonia, hydrocyanic acid, naphthalene, tar-fog, oxides of nitrogen, sulphur dioxide, and hydrogen phosphide.

Ethylene.

The following is the method devised by Haber and V. Oechelhäuser[1] for estimating ethylene and, indirectly, benzene in coal gas by the use of bromine (see also p. 241).

About 90 c.c. of the gas is run into a Bunte burette, the confining water sucked out in the usual manner, and a standard solution of bromine water (about half saturated) allowed to run into the burette up to a definite mark, which is noted (*e.g.*, the 5 c.c. mark). A little water is then allowed to enter to clear the capillary tube and stopcock of bromine water, and the burette shaken for two minutes, after which the

[1] *J. Gasbeleucht.*, 1900, **43**, 347.

colour of bromine vapour should still be distinctly visible. After a further three minutes, a solution of potassium iodide is sucked into the burette, the latter washed out with water, and the iodine liberated by the unaltered bromine titrated with sodium thiosulphate and starch. A blank test of the bromine water is made by drawing up some of the solution to the same mark as before, adding potassium iodide, and titrating the solution. The difference in the quantities of $N/10$ thiosulphate used in the two tests gives the amount of bromine which has combined chemically with the ethylene; 1 c.c. of $N/10$ thiosulphate corresponds to 1·2 c.c. of ethylene at 15° and 760 mm., or 60° F. and 30 in.

Homologues of ethylene, if present, also combine with bromine, but as unit volume of any olefine combines with the same quantity of bromine, the total volume of olefines is correctly given by the test. Unsaturated hydrocarbons of other series, such as acetylene and its homologues, interfere with the results, as these absorb a much larger amount of bromine. For coal gas the amount of such hydrocarbons is too small to have a material effect, but according to Fritzsche,[1] they are present in oil gas in considerable quantity, and the method is not applicable to such gases.

Benzene.

The method of volumetric estimation by means of ammoniacal nickel cyanide has been described (p. 242), but sufficient experience has not yet been gained with the process under varying conditions to judge of its reliability. When the ethylene has been determined by the method described above and the total percentage of heavy hydrocarbons by absorption with bromine or fuming sulphuric acid, that of benzene is given by the difference of the two values.

The most suitable method for the determination of benzene, etc., in coal gas is probably that devised by St Claire Deville[2] and recently modified by him so as to make it applicable to gas containing small quantities of benzene.[3] The amount of benzene and its homologues is determined by passing the dried gas through a glass cooling coil immersed in a mixture of ice and salt so that the gas is cooled to $-22°$; the condensed hydrocarbons are collected in a tube and weighed. A correction is made for the benzene still left in the gas at this temperature. This amounts to 23·5 g. of benzene per cubic metre (0·67 g. or 10·33 grains per cubic foot).

When the gas contains very little benzene, it is dried by means of calcium chloride and then cooled to $-72°$ by passing through a condenser immersed in carbon dioxide snow in a Dewar flask. At

[1] *J. Gasbeleucht.*, 1902, **45**, 281.
[2] *J. Gasbeleucht.*, 1899, **42**, 652.
[3] *J. des Usines à Gas*, 1918; *Gas Journal*, 1919, pp. 145, 272.

this temperature the vapour pressure of benzene and other aromatic hydrocarbons is practically nil. The vapours are therefore all condensed, and the residual gas may be measured by means of an ordinary meter; the weight of crude benzene per unit volume of gas measured at 10° and 760 mm. pressure is calculated after allowing for the volume of vapour condensed. In the case of coal gas, this is assumed to be 1 litre per 3·73 g. (based on 3 vols benzene + 1 vol toluene).

Harbeck and Lunge[1] have described a method of determination by conversion into dinitrobenzene which has been much simplified by Pfeiffer.[2] The latter converts the benzene vapour into dinitrobenzene by treating about 500 c.c. of the gas, contained in a separating funnel, with sulphuric and nitric acids, and estimates the dinitrobenzene produced by titration with stannous chloride according to Limpricht's method.[3]

H. S. Davis and M. D. Davis[4] have employed a differential pressure method for the quantitative determination of vapours in gases. Two flasks connected to the limbs of a delicate differential pressure gauge are employed. One flask is filled at atmospheric pressure with gas containing the vapour the amount of which is to be determined. The other flask is filled at the same pressure with gas from which the vapour is absent. The gas in each flask is now saturated with the vapour in question. The differential pressure indicated by the gauge is a measure of the partial pressure of the vapour originally in the gas.

For most gas works purposes, the determination of benzene is rarely required, but in coke oven works, where the gas made is frequently washed with tar oils to recover the vapours of benzene and its homologues, a knowledge of their amount is desirable. The method usually adopted is to pass from 40 to 100 cb. ft. of gas through a series of four bottles, each charged with about 150 c.c. of heavy tar oil, which has been previously distilled till the thermometer in the vapour reaches 270°. The gas is bubbled through the bottles at a rate not much exceeding 1 cb. ft. per hour, and when the required amount of gas has been passed, the combined oil from the flasks is distilled, using a 3-bulb Le-Bel-Henninger fractionating column, the distillation being continued up to 140°, and the distillate collected in a measuring cylinder. This consists chiefly of benzene with smaller quantities of toluene and xylenes. The method is, of course, not a very exact one, but gives results which agree fairly closely with the yields actually obtained on the large scale in the extraction of the benzene hydrocarbons.

[1] *Z. anorg. Chem.*, 1898, **16**, 41.
[2] *J. Gasbeleucht.*, 1899, **42**, 697; *Chem. Zeit.*, 1904, **28**, 884.
[3] *Ber.*, 1878, **11**, 35.
[4] *J. Ind. Eng. Chem.*, 1918, **10**, 709.

Vapours of higher boiling liquids in the gas may be estimated approximately in a similar manner, by passing about 100 cb. ft. through a train of wash-bottles containing heavy oils previously freed from low-boiling constituents. The contents are then distilled till the thermometer reaches 270°, and the distillate fractionated, using a 3-bulb Le-Bel-Henninger column, and the volume of distillate for each 10° interval, up to 210° measured.

Rhead[1] describes a washing tower containing a number of trays, for the extraction and determination of benzene. Creosote or other oil of low volatility enters the top tray from a constant-head feed, gravitates from tray to tray through sealed pipes and finally collects in a receiver at the base of the tower. The gas after passage through a meter passes upwards through the tower and is caused to bubble through the oil in each tower by means of hoods with serrated edges. About 4 litres of oil are required to extract the benzene and toluene from 100 cb. ft. of coal gas. Crude benzene is recovered from the washing oil by steam distillation, and determined.

Lessing[2] packs a scrubbing tower with pieces of inert material such as porous brick, soaked in an oil of such viscosity that it is not unduly thinned or washed out by the solvent vapours derived from the gas. Very little resistance is offered to the flow of the gas, and the device permits of benzene, etc., being recovered by steam distillation without removal of the absorbent from the tower. A device in which the gas to be washed is passed through a mass of condensing vapour has been described by Gray.[3]

Lebeau and Damiens,[4] and Burrell, Siebert, and Robertson[5] employ methods depending upon the fractional distillation of liquefied coal gas. The methods are especially applicable to the determination of compounds, such as thiophen, present in coal gas only to a small extent. Such constituents are condensed and held in solution by benzene or other added solvent.

Acetylene.

This hydrocarbon is present in coal gas only in small quantity, generally not exceeding 0·1 per cent. The gas, purified if necessary from sulphuretted hydrogen, is passed through two Volhard absorbing bottles, each charged with 20 c.c. of concentrated ammoniacal silver nitrate solution, which absorbs the acetylene with formation and precipitation of silver acetylide, some silver being also formed by the reducing action of other constituents of the gas. The filtered and

[1] *J. Soc. Chem. Ind.*, 1917, 36, 767.
[2] *J. Soc. Chem. Ind.*, 1917, 36, 103.
[3] *J. Chem. Soc.*, 1917, 111, 179.
[4] *Comptes rend.*, 1913, 156, 144 and 325.
[5] *U.S. Bureau of Mines*, Tech. Paper No. 104, 1915.

washed precipitate is cautiously treated with dilute hydrochloric acid on the filter till acetylene ceases to come off, the resulting mixture of silver chloride and silver digested with ammonia, filtered, the precipitate washed with ammonia, and the combined filtrates treated with nitric acid to precipitate the silver chloride, which is filtered off, and weighed; 1 g. of silver chloride corresponds to 0·09072 g. or 84·03 c.c. of acetylene measured moist at 15° and 760 mm.

Oxygen.

The technical importance of the determination of oxygen in coal gas arises more especially in the purification of illuminating gas from sulphuretted hydrogen by means of oxide of iron. In order to increase the rate of purification and to revivify the oxide *in situ*, air is customarily admitted to the purifiers along with the gas. The most suitable proportion depends upon local circumstances, but, as a general rule, it is found that the average percentage of oxygen should be rather more than half the average percentage of sulphuretted hydrogen.

The Haldane gas analysis apparatus (p. 289 *et seq.*) can be readily adapted to determine with accuracy the oxygen content of the gas before or after purification. Carbon dioxide and heavy hydrocarbons are first removed by potash solution and bromine (pp. 241, 243) respectively, and oxygen subsequently determined by absorption with alkaline pyrogallate in the usual manner.

A colorimetric method of estimation has been devised by Pfeiffer,[1] depending on the depth of colour produced by a known volume of the gas in an alkaline solution of pyrogallol, this being compared with standards of iodine in potassium iodide solution made up to match the colours given by known percentages of oxygen. Lubberger[2] has applied Winkler's method for estimating dissolved oxygen in water to the estimation of oxygen in coal gas, the gas being shaken in a Bunte burette with alkali and manganous hydroxide in oxygen-free water, the manganese being oxidised to hydrated peroxide. The latter is then treated with potassium iodide and hydrochloric acid, and the liberated iodine, equivalent in amount to the oxygen taken up by the manganous hydroxide, is estimated by $N/100$ sodium thiosulphate in the usual manner.

The purity of technically prepared oxygen is determined as described on p. 246 by the use of copper wire kept clean and moist by a solution composed of equal volumes of ammonia and of saturated ammonium carbonate solution.

[1] *J. Gasbeleucht.*, 1897, **40**, 354. [2] *Ibid.*, 1898, **41**, 695.

Carbon Dioxide.

The estimation of this constituent in illuminating gas by absorption with aqueous potassium hydroxide is not very accurate, as this reagent also tends to absorb some of the hydrocarbon vapours present. When greater accuracy is required, gravimetric or volumetric methods are employed; the former are carried out by absorbing the carbon dioxide in a weighed soda-lime tube, and the latter by treatment of the gas with standard baryta water by Pettenkofer's method. In the former method, the gas, if unpurified, must be first freed from ammonia by passing through dilute acid, and from tar-fog and sulphuretted hydrogen, by passing through a tower filled with hydrated ferric oxide. The gas is then led through the meter, dried by calcium chloride, and passed into the weighed soda-lime tube, the last part of which is charged with calcium chloride to prevent loss of moisture. Each gram of CO_2 found corresponds to 544 c.c. of the gas measured moist at 15° and 760 mm.

FIG. 163.

For the estimation by means of baryta water, a convenient method is to employ a bottle of about 2 litres capacity, having a doubly bored rubber cork fitted with a small separating funnel of about 50 c.c. capacity, and a right-angled delivery tube as shown in Fig. 163. The exact capacity of the bottle is determined by weighing it empty and then filled with water, the delivery tube being removed, and the stem of the funnel filled with water up to the stopcock; the difference of weight in grams gives the volume in cubic centimetres. To fill the bottle with saturated gas, one or two drops of water are added, the apparatus inverted, and gas passed in through the separating funnel and out through the delivery tube; two to three minutes' passage of a moderate stream of gas suffices to drive out all air. The delivery tube is then removed, replaced by a glass plug, the separating funnel stopcock closed, and the gas shut off and disconnected. The stopcock is then again opened for a second to allow the gas in the bottle to attain atmospheric pressure, and the height of the barometer and the room temperature noted.

As soon as the gas in the funnel has been replaced by air, 50 c.c. of baryta water of known strength (20 g. barium hydroxide per litre) and a little phenolphthalein are run into the funnel, and thence, by careful opening of the cock, into the bottle, cooling under the tap, if necessary, to create a slight vacuum; the funnel is then washed out with water into the bottle, care being taken that the stem of the funnel is left full of water. The bottle is well shaken, and allowed to stand for ten minutes, when absorption is complete. The stopcock is

then opened, the contents of the bottle, including the precipitate, washed out into a flask, and titrated at once with $N/10$ oxalic acid, using phenolphthalein as indicator. Fifty c.c. of the original baryta solution are titrated in the same manner; the difference between the quantity of oxalic acid solution required for neutralisation represents the amount of alkali corresponding to the carbon dioxide absorbed, expressed in decinormal solution; each cubic centimetre of $N/10$ oxalic acid corresponds to 0·0022 g., or to 1·119 c.c. of dry CO_2 at 0° and 760 mm. To obtain the percentage of the gas, the volume of CO_2 under these conditions must be converted in the usual manner into the volume of moist gas measured at the same temperature and pressure as observed with the volume of gas taken. If n equals the number of cubic centimetres of $N/10$ oxalic acid found, v the capacity of the bottle in cubic centimetres, t the temperature, s the vapour pressure of water at that temperature, and b the height of the barometer, the percentage of CO_2 is found by the equation :—

$$\text{Percentage of } CO_2 = \frac{n \times 1.119 \times (273+t) \times 760 \times 100}{273 \times (b-s) \times v}$$

$$\begin{array}{ccc} & \textit{Constants.} & & \textit{Variants.} \\ = & \dfrac{1.119 \times 760 \times 100}{273 \times v} & \times & \dfrac{n \times (273+t)}{b-s} \end{array}$$

When v has been determined, a simple figure for the constants can be calculated once for all.

The determination of carbon dioxide can also be readily made and recorded by means of the katharometer and other devices (see p. 321 *et seq.*).

Carbon Monoxide.

The determination of small quantities of carbon monoxide is often of extreme importance. The detection and approximate quantitative determination of small proportions of this gas can be effected either by its reducing action on palladious chloride, blood, or iodine pentoxide (p. 262). The flame-cap test is also applicable. These methods are described in detail in the section on "Air Analysis," Vol. III.

Hydrogen Sulphide.

According to Haldane,[1] hydrogen sulphide in very great dilution is readily recognised by its characteristic smell. This test is less distinctive when the proportion of hydrogen sulphide present exceeds 0·01 per cent., but then irritation of the eyes is produced.

For the control of the purification process in gas works, the estima-

[1] *The Investigation of Mine Air*, Foster and Haldane, 1905, p. 149.

tion of sulphuretted hydrogen by volumetric absorption with a solution of cadmium sulphate or chloride gives results of sufficient accuracy. For more accurate determinations, especially when only small quantities are present, other methods must be employed. The gas tested must be freed from tar-fog and ammonia, if present; the former is removed by a small cotton-wool filter, and the latter by washing with dilute sulphuric acid.

(i.) *Gravimetric Estimation.* For this purpose, Fresenius[1] employs as absorbent, pumice stone which has been treated with saturated copper sulphate solution, dried, and heated for four hours at 250°. According to L. T. Wright,[2] copper phosphate is a more suitable absorbent. To prepare it a solution of 100 g. of crystallised sodium hydrogen phosphate in 500 c.c. of water is added, with constant stirring, to a solution of 125 g. of crystallised copper sulphate in 750 c.c. of water, the precipitated phosphate being filtered off and dried at 100°. Either absorbent is placed in a U-tube so as to occupy about five-sixths of its length, the remaining one-sixth being filled with calcium chloride. The gas is dried by calcium chloride, and passed through the weighed U-tube containing the copper sulphate or phosphate, and thence through a meter or into a graduated aspirator. At the end of the test, dry air is drawn through the U-tube, which is then weighed, the increase of weight giving the weight of H_2S in the volume of gas passed. One gram of H_2S equals 697·6 c.c. or 0·02464 cb. ft. of moist gas at 15° and 760 mm.

(ii.) *Volumetric Estimation.* The most suitable reagent is a standard solution of iodine in potassium iodide, which reacts with sulphuretted hydrogen yielding sulphur and hydriodic acid, according to the equation:—

$$H_2S + I_2 = 2HI + S.$$

This reaction may be carried out in a Bunte burette,[3] using a solution of iodine in potassium iodide containing 1·0526 g. of iodine per litre, 1 c.c. of which = 0·1 c.c. of H_2S measured moist at 15° and 760 mm. The gas to be tested, after being freed from tar-fog and ammonia, is passed into the completely dry burette (if necessary with the assistance of an aspirator), and a portion of the gas then sucked out to make room for the reagents. The iodine solution is then sucked in from a small dish so as to fill the capillary and bore of the stopcock, and then starch solution to the lowest division mark. By gradually adding fresh quantities of iodine, and repeated shaking, the end-point of the reaction is recognised by the usual formation of a permanent blue colour.

[1] *Quantitative Analysis*, 7th ed., vol. i., p. 383.

[2] *J. Soc. Chem. Ind.*, 1885, **4**, 665.

[3] *Cf.* Bunte, *J. Gasbeleucht.*, 1888, **31**, 899; Kast and Behrend, *ibid.*, 1889, **32**, 159.

The amount of iodine used is read off directly on the burette, the amount remaining in the capillary being balanced by that added before the starch, which is not measured. The volume of gas used is then determined in the usual manner.

An alternative method consists in employing a dry bottle of known capacity (about 500 c.c.) closed with a hollow stopper capable of holding 25 c.c. (A glass tube of this capacity, closed at one end and fitted into a rubber cork the bottom of which is coated with a film of paraffin wax, may be substituted for a ground-in stopper.) The gas, purified from tar-fog and ammonia, is blown through the inverted bottle till all air is driven out; the tube or stopper, to which 25 c.c. of *N*/10 iodine solution has been added, inserted whilst the bottle is still inverted, and the solution shaken with the gas; the contents of the bottle and stopper are then washed out, and the excess of iodine determined by titration with sodium thiosulphate and starch. Each cubic centimetre of iodine used equals 1·122 c.c. of dry H_2S at 0° and 760 mm.; the percentage of the gas is calculated in exactly the same manner as that of carbon dioxide given on p. 303, with the substitution of the figure 1·108 for that of 1·119 in the equation.

The iodine method is likely to give high results, since the unsaturated compounds and also hydrocyanic acid, when present in the gas, tend to combine with iodine. With coal gas the error thus caused is usually small, but it is very considerable in the case of oil gas and of carburetted water gas, owing to the presence of cyclopentadiene, C_5H_6.[1]

C. W. Somerville[2] has described a modified iodometric method in which the gas is drawn by means of an aspirator through a wash-bottle of 100 c.c. capacity containing 10 c.c. of *N*/1000 iodine solution and 10 c.c. of specially prepared starch solution diluted to 100 c.c. The passage of the gas is continued until the blue coloration just disappears, the volume of gas used being found from the volume of water run off from the aspirator. To obviate the error due to the above-mentioned impurities, a second test is made with the same gas, which is first passed through a small tower containing lead carbonate to remove sulphuretted hydrogen; by deducting the second result from the first the true amount of sulphuretted hydrogen is found.

(iii.) *Colorimetric Estimation.* The colorimetric method devised by Vernon Harcourt (see p. 308) is very convenient for the estimation of sulphuretted hydrogen, especially where this impurity is present only in small quantity. In this process the gas is bubbled in a fine stream through a standard sized tube containing a solution of lead acetate in

[1] *Cf.* also, Ross and Race, *J. Soc. Chem. Ind.*, 1910, **29**, 604.
[2] *J. Gas Lighting*, 1910, **112**, 29.

excess of sodium hydroxide, to which sugar is added, the passage of the gas being continued until the solution attains the same brown colour as the similar sized standard tube (see Fig. 164, p. 307), which is artificially made to correspond with the colour given to the standard lead solution by 0·0025 grains (0·000162 g.) of sulphur, by mixing solutions of copper, cobalt, and ferric sulphates. The gas is drawn through the solution by an aspirator, which is completely filled with water at the commencement, the water run out being collected in a measuring cylinder, thus giving a direct reading of the volume of gas passed. This volume of gas therefore contains the above quantity of sulphur as sulphuretted hydrogen, and from this figure either the percentage, or amount in any given volume, is readily calculated.

The brown solution becomes colourless on exposure to light, and provided that carbon dioxide is excluded the revivified solution may be used again for a considerable number of estimations.

Well-prepared "lead-paper" is an exceedingly delicate agent for the detection of minute traces of hydrogen sulphide. The most satisfactory papers are prepared by moistening sheets of filter paper with a solution of 1 part of sugar of lead in 8 or 9 parts of water, and holding each sheet while still damp over the surface of a strong solution of ammonia for a few minutes. The ammonia escapes as the paper dries. When such papers are immersed for, say, half an hour in a large volume of gas, very minute traces of sulphuretted hydrogen will give a brown stain. Light should be excluded from the vessel during the test. It is often convenient for the gas to issue from a small orifice and impinge directly upon the test paper. The delicacy of the test is increased by using a moist test paper. Attempts have been made to determine a scale enabling the percentage of hydrogen sulphide present to be ascertained from the colour imparted to the test paper after passage of a definite volume of gas. When a paper is exposed to a slow stream of gas after the manner prescribed by the Gas Referees, 1 part of hydrogen sulphide per million is readily detected in three minutes. Lehmann states that after passage of 8 litres of air at the rate of 12 litres per hour through a tube 12 mm. in diameter, the paper being held at the outlet of the tube, a pale brown colour is formed when hydrogen sulphide is present to the extent of 0·0001 per cent. to 0·0002 per cent. A strong yellowish brown colour is obtained when the percentage present is 0·0003 per cent., while 0·0005 per cent. gives a dark brown colour, and 0·0008 per cent. a brownish black colour. According to Butterfield,[1] the two sides of a piece of lead acetate paper $\frac{1}{12}$ sq. in. in area, become something approaching light oak colour when brought in contact with 0·007 c.c. of hydrogen sulphide.

[1] *Chemistry in Gas Works*, 1913, p. 56.

Sulphur Compounds other than Hydrogen Sulphide in Coal Gas; Carbon Bisulphide; Total Sulphur Compounds.

Coal gas purified by means of oxide of iron, always contains small quantities of volatile sulphur compounds other than sulphuretted hydrogen. The vapour present in largest quantity is that of carbon bisulphide, the amount of which varies from 10 to 80 grains per 100 cb. ft., according to the variety of coal carbonised and the conditions of distillation. From 5 to 10 grains of sulphur is also present in the form of other compounds, among which thiophene, carbonyl sulphide, and alkyl mercaptans and sulphides have been detected.

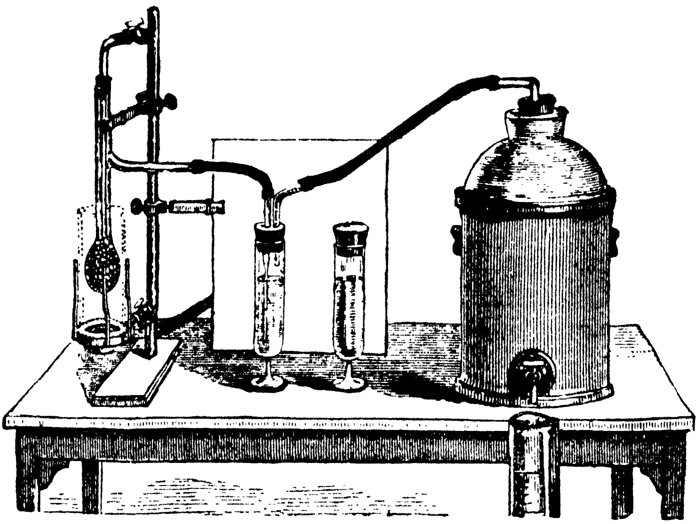

FIG. 164.

For the estimation of *carbon bisulphide*, a measured volume of the gas freed from sulphuretted hydrogen, if necessary, by iron oxide, is dried by calcium chloride and passed through two wash-bottles containing a solution of potassium or sodium hydroxide in absolute alcohol, which converts the bisulphide into potassium or sodium xanthate according to the equation :—

$$CS_2 + KOH + C_2H_5OH = CS\begin{matrix} \diagup SK \\ \diagdown OC_2H_5 \end{matrix} + H_2O.$$

Both gas and reagent must be kept as dry as possible, as water decreases the absorbing power of the reagent for the bisulphide. The quantity of xanthate or of sulphur in the solution obtained may then be ascertained by the methods used for the estimation of carbon bisulphide in commercial benzene (see under "Coal Tar," Vol. IV.).

The carbon bisulphide may also be estimated by Harcourt's colorimetric method. When coal gas containing carbon bisulphide is passed over platinised pumice, the bisulphide is converted into sulphuretted hydrogen, which is then estimated colorimetrically in the manner described under sulphuretted hydrogen (p. 305 *et seq.*). To carry out the test, a small fractionating flask of about 30 c.c. capacity filled with platinised pumice is placed in a special stand surrounded by a glass chimney (Fig. 164), so that the bottom of the flask is about 1 in. above the small ring burner fixed at the bottom of the chimney. The burner is lighted, turned down until the flame just shows a slight luminosity, thus heating the platinised pumice to 300°-350°. The gas is then allowed to pass through at the rate of about 0·5 cb. ft. per hour.

After about ten minutes, the delivery tube is connected to the tube containing lead acetate syrup, and the latter to an aspirator, and the gas drawn in a thin stream through the tube until the same depth of colour is obtained as in the standard cylinder, corresponding to 0·0025 grain or 0·000162 g. of sulphur. The volume of gas containing this quantity of sulphur as carbon bisulphide is that of the water run from the aspirator and collected in the measuring cylinder.

This method, though very rapid and convenient, only gives results of fair accuracy if the gas tested is free or almost free from oxygen. Mostly, however, purified coal gas contains appreciable quantities of oxygen, which in presence of the hot platinised pumice converts the sulphuretted hydrogen into sulphur and water; the results then obtained are much below the true figure.

The separate determination of carbon bisulphide is seldom carried out, as all the information usually required is obtained by the estimation of the *total sulphur* present, by burning a known volume of gas and estimating the sulphur in the products of combustion.

In this country the method almost always employed is that specified by the Gas Referees; it is generally known as the "Referees" method. The gas is burnt in a small Bunsen burner with a steatite top (Fig. 165), which is mounted on a short cylindrical stand, perforated with holes for the admission of air, and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of the glass trumpet tube. There are, both on the side and on the top of the stand, fourteen holes 5 mm. in diameter, or an equivalent air-way. On the top of the stand, between the narrow stem of the burner and the surrounding glass trumpet tube, are placed pieces of commercial sesquicarbonate of ammonia weighing in all about 2 oz. The products of combustion and of the gradual volatilisation of the sesquicarbonate pass upwards through the trumpet tube into a vertical glass cylinder with a tubulure near

the bottom, and drawn in at a point above this to about half its diameter. The cylinder is packed, from the contraction to the top, with balls of glass about 15 mm. in diameter, to break up the current and promote condensation. From the top of this condenser there proceeds a long glass pipe or chimney tube slightly bent over at the upper end, serving to effect some further condensation as well as to regulate the draught and afford an exit for the uncondensed gases. The chimney tube is suspended by a tape, tied round the middle of it, and attached above to a bracket projecting from the wall. At the bottom of the condenser is fixed a small glass tube drawn out to a jet through which the liquid formed during the test drops into a flask beneath.

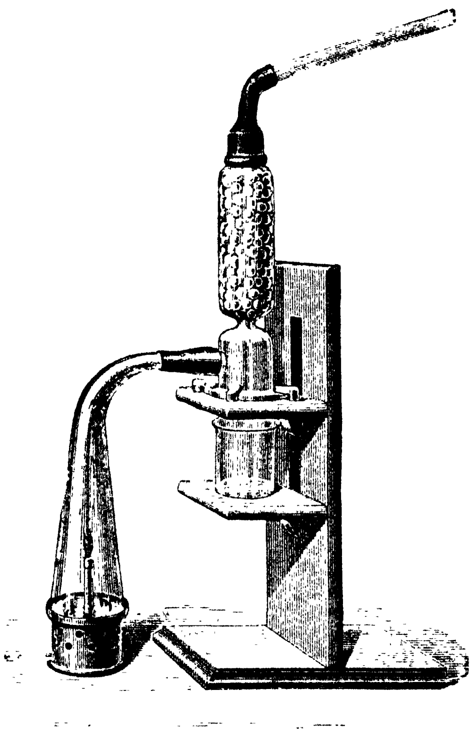

FIG. 165.

After each test, the flask or beaker which has received the liquid products of the combustion of 6 cb. ft. of gas is emptied into a measuring cylinder and then replaced to receive the washings of the condenser. The trumpet tube is then removed and well washed out with distilled water into the measuring cylinder. The condenser is flushed two or three times by pouring quickly into the mouth of it 40 or 50 c.c. of distilled water. These washings are brought into the measuring cylinder, the whole contents being then well mixed.

An aliquot part of the liquid is placed in a flask or beaker, covered with a large watch-glass, and acidified with hydrochloric acid. The sulphur present is then precipitated by hot barium chloride in the usual way.

The correction of the gas volume to 60° F. and 30 in. pressure is found by the table on pp. 238, 239.

The method tends to give slightly low results owing to incomplete oxidation of the sulphites to sulphates. To avoid this possibility, some analysts prefer to oxidise the solution with bromine water before precipitation, whilst others oxidise with nitric acid, and precipitate with

barium nitrate instead of chloride. T. Fairley[1] dispenses with the use of ammonium carbonate, and allows a solution of hydrogen peroxide to drip down the condensing cylinder of the Referees' apparatus, the sulphur being then obtained in the condensate as free sulphuric acid. The amount of sulphuric acid may then be determined by titration with normal alkali, provided that the hydrogen peroxide solution used is neutral. Or, by using a known volume of hydrogen peroxide solution of determined acidity, the sulphuric acid formed may be found by deducting the amount of the latter from the total quantity of acid found.

H. Blair[2] has proposed the following volumetric method for the estimation of the sulphuric acid in the solution obtained by the Referees' process. An aliquot portion of the solution is boiled to volatilise the ammonium carbonate, thus leaving neutral ammonium sulphate; an excess of neutral formaldehyde solution (about 30 per cent.) is then added to the hot solution. It reacts with the ammonia, forming hexamethylene-tetramine, and liberates sulphuric acid, in accordance with the equation :—

$$4(NH_4)_2SO_4 + 6CH_2O = N_4(CH_2)_6 + 2H_2SO_4 + 6H_2O.$$

The liberated sulphuric acid is then determined by titration with $N/10$ alkali, using phenolphthalein as indicator; 1 c.c. $N/10$ alkali = 0·0247 grain S.

In the method due to Drehschmidt,[3] the estimation is carried out by means of the apparatus shown in Fig. 166. The gas burner is encased in the manner shown in the figure, separate pipes, *a* and *b*, projecting from the casing for the supply of gas and air respectively to the burner. The air supply is purified from any sulphur dioxide present by passing up the tower B, containing pumice moistened with aqueous potassium hydroxide. The glass cylinder C is placed over the burner and fits a circular channel in the burner case, filled with mercury, thus preventing the admission of air at this point. The glass tube fused on to the cylinder C conveys the products of combustion to the train of wash-bottles D, each containing 20 c.c. of aqueous potassium hydroxide (5 per cent.), a little bromine being added in the first two bottles to ensure the complete oxidation of the sulphur dioxide.

In making a test, the burner is lighted and regulated to a consumption of $\frac{2}{3}$ to 1 cb. ft. per hour; the outlet of the last wash-bottle is connected to a powerful water-pump so that a rapid current of air is drawn through the apparatus. The cylinder C is placed over the burner as the hand of the meter passes a suitable point, when the flame continues to burn quietly if the current of air is sufficiently rapid. At

[1] *J. Soc. Chem. Ind.*, 1887, **5**, 283. [2] *Ibid.*, 1911, **30**, 397.
[3] Post's *Chemisch-Technische Analyse*, 1888.

the conclusion of the test the contents of the bottles D are washed out and the sulphur estimated as barium sulphate in the usual manner.

In place of the sodium hypobromite solution, hydrogen peroxide may be used in the wash-bottles, and the amount of sulphuric acid produced determined by titration with alkali, as described on p. 310. Pfeiffer employs a modified method in which the products

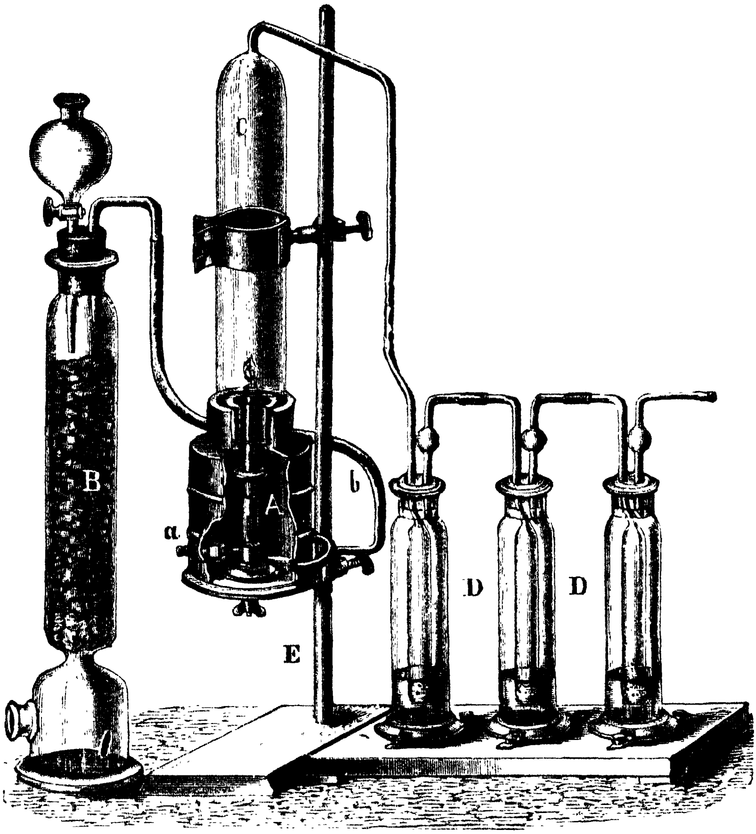

FIG. 166.

of combustion are drawn through a known volume of decinormal sodium hydroxide solution to which neutral hydrogen peroxide solution (Merck's perhydrol) is added. The amount of alkali remaining at the end of the test is determined by titration with $N/10$ sulphuric acid, using dimethylaminoazobenzene as indicator. Each c.c. of $N/10$ alkali neutralised is equivalent to 0·001603 g. or 0·02478 grain of sulphur, and the number of grains of sulphur per 100 cb. ft. is obtained by the equation :—

$$\text{grs. per 100 cb. ft.} = \frac{\text{Number of c.c. } N/10 \text{ NaOH} \times 0.02478 \times 100}{\text{Gas consumed corrected to N.T.P.}}$$

A quick method for the estimation of total sulphur, especially suitable for works, has been published by C. W. Somerville;[1] it depends on the estimation of the sulphur dioxide in the products of combustion of the gas by means of iodine and starch. The apparatus[2] in general construction resembles that of Drehschmidt (Fig. 166, p. 311), the gas being burned at the rate of about 0·5 cb. ft. per hour from a small burner, and the products of combustion aspirated by means of a water-pump through a wash-bottle of about 500 c.c. capacity containing 100 c.c. of $N/1000$ iodine solution diluted to 450 c.c., and a few cubic centimetres of starch solution. The wash-bottle is connected to the cylinder covering the flame as the meter hand passes a noted point, and the combustion products are allowed to pass through the solution until it is just decolorised, when the gas meter is at once bypassed. One hundred c.c. of $N/1000$ iodine contain 0·1269 g. of iodine, equivalent to 0·0016 g. or 0·024688 grain of sulphur, which is, therefore, the amount present in the volume of gas burned; from this the quantity of sulphur in 100 cb. ft. is readily calculated.

Ammonia.

Of the total nitrogen present in coal, only some 10 to 14 per cent. is obtained in the crude coal gas in the form of ammonia; the bulk of the remainder remains in the coke, and smaller quantities are obtained as gaseous hydrocyanic acid, free nitrogen, and as compounds of nitrogen with carbon and hydrogen, such as pyridine and quinoline, which are found in the tar.

The removal of the ammonia from the crude gas commences as soon as the temperature has been sufficiently lowered to permit of the condensation of steam to water, and about one-half of the ammonia present is usually removed in the hydraulic main and condensers, the remainder being recovered by washing with weak liquor or fresh water in the washers or scrubbers. Where the latter part of the process is efficiently worked, the ammonia is reduced at the outlet of the apparatus to from 0·5 to 2·0 grains per 100 cb. ft.

The ammonia present is readily determined by passing a measured volume of gas through two absorption bottles in series, each containing a measured volume of normal or decinormal sulphuric acid, and determining the excess acid at the end of the test by titration with standard alkali, using methyl orange as indicator. A tube filled with broken glass, and moistened with a known volume of standard acid, may be used in place of the absorption bottles; but care must be taken, by making a blank test, that the glass has not an alkaline reaction;

[1] *J. Gas Lighting*, 1910, **112**, 29.
[2] Supplied by Messrs Townson & Mercer, Camomile St., London, E.C.

the glass beads supplied with such apparatus are often strongly alkaline, thus rendering the results obtained much too high.

With purified gas containing only a few grains of ammonia per 100 cb. ft., decinormal acid is used, and very accurate results are obtained, if the tubes leading to the absorption bottles are of glass, with only a minimum of rubber connecting tubing.

For crude unscrubbed gas, normal acid must be employed, and the above-named precautions are especially necessary; the gas should be sampled by means of a tube projecting into the main, as described on p. 297. Exact results are somewhat difficult to obtain on account of the tar-fog present in the gas, which makes the end-point of the titration difficult to observe, and the ammoniacal liquor particles carried mechanically with the fog also neutralise some of the acid, thus making the results too high. If, on the other hand, an attempt be made to remove the tar-fog by a cotton-wool filter, the results are too low, as the filter also effects the removal of some of the ammonia from the gas stream. On the whole, it is best not to attempt to remove the tar-fog, but to allow for the fact that the tendency is then for the results to be rather too high.

When tar is present, it is sometimes found that the use of fluorescein as indicator, in place of methyl orange, is advantageous; the point of neutralisation is recognised by the disappearance of fluorescence, which is most readily observed if the glass vessel containing the liquid be placed on a sheet of glazed black paper.

With crude gas containing large quantities of ammonia, the small quantity of gas required for a test is often conveniently measured by a graduated aspirator instead of by a meter; where the gas to be tested is under a pressure less than that of the atmosphere, the suction of the aspirator is utilised to draw the gas from the main through the absorption bottles. Where a meter is used, and the gas contains sulphuretted hydrogen, a small oxide purifier should be placed between the absorption bottles and the meter, to prevent corrosion of the metal work.

Traces of ammonia are readily determined by the use of either turmeric or hæmatoxylin paper, or paper saturated with Nessler's solution. Turmeric paper is prepared by impregnating bibulous paper with an alcoholic solution of turmeric. The paper is turned reddish brown by ammonia, but is bleached by hydrogen sulphide. Hæmatoxylin paper, when dry, is slightly yellow or pink. It becomes blue in the presence of alkalis, and is extremely sensitive to ammonia.

Nessler's solution may be employed for the exact determination of a minute trace of ammonia in air or other gas. A definite volume of the gas is passed into water slightly acidified with sulphuric acid, the absorbed ammonia being subsequently determined colorimetrically in the usual way (see Vol. III. under "Water Analysis").

Hydrocyanic Acid.

For the determination of hydrocyanic acid in coal gas, two methods are employed:—

(i.) The gas is passed through a series of two or more absorption bottles, charged with a mixture of ferrous hydroxide and potassium hydroxide, prepared by mixing equal volumes of ferrous sulphate solution (1 : 10) and potassium hydroxide solution (1 : 3), the gas being passed at a rate of about 1 cb. ft. per hour, and measured in a meter in the usual manner. The contents of the absorption bottles are washed out at the end of the test, made up to a known volume, and an aliquot portion of the shaken mixture filtered from the insoluble black residue, which is washed free from ferrocyanide. The filtrate is treated with lead carbonate to remove sulphides, and the filtered solution heated to 60°, and precipitated with hydrochloric acid and excess of ferric chloride; the precipitated Prussian blue is then filtered off, decomposed, and analysed as described in the section on "Cyanogen Compounds," p. 630 *et seq.*

(ii.) In the second method, the hydrocyanic acid is absorbed by passing the gas through a series of three absorption bottles charged with a solution of ammonium sulphide and free sulphur; the ammonium polysulphide formed combines with the hydrocyanic acid, with the formation of ammonium thiocyanate. The gas is passed at the rate of about 1 cb. ft. per hour, and is measured as usual. At the end of the test the contents of the bottles are washed out, made up to a known volume, an aliquot portion of the solution treated with lead carbonate to remove sulphides, and, after filtering, a few crystals of sodium sulphite added, and the whole heated to 80°; the liquid is then made faintly acid with sulphuric acid, and precipitated with an excess of copper sulphate solution, which throws down cuprous thiocyanate as a white precipitate, accompanied, however, by sulphides of copper, formed by the decomposition of the thiosulphate also present. The precipitate is filtered immediately, washed once or twice with water, and decomposed by the addition of 10 c.c. of a 10 per cent. solution of sodium hydroxide, free from chlorides. The sodium thiocyanate solution produced is filtered from the cuprous hydroxide and sulphide, the latter washed, the cold filtrate acidified with dilute nitric acid, and titrated with $N/10$ silver nitrate solution using ferric alum solution as indicator, the complete precipitation of the thiocyanate being shown by the disappearance of the red colour of the ferric salt. Each c.c. of $N/10$ $AgNO_3 = 0{\cdot}007612$ g. of NH_4CNS, or 0·002703 g. of HCN.

The precipitation of the cuprous thiocyanate is necessary to remove the thiosulphates always present in the solution, and which if not eliminated, would also be precipitated by the silver nitrate. For most

purposes this may be done more quickly and with sufficient accuracy, by the method proposed by Linder.[1] In this procedure the solution, after removal of sulphides by lead carbonate, is slightly acidified with sulphuric acid, heated to boiling, and 10 c.c. of a saturated solution of ferric alum added; after standing for five minutes, the liquid is cooled, acidified with nitric acid, and titrated with decinormal silver nitrate. The ferric alum converts the thiosulphate into tetrathionate, which does not affect the silver nitrate if the titration is carried out quickly.

The ferrocyanide method tends to give results which are slightly low, as small quantities of the hydrocyanic acid are always converted into thiocyanate instead of into ferrocyanide, the amount of thiocyanate formed being greater when ammonia is present in the gas. On the other hand, the thiocyanate method tends to give results rather above the truth, as the carbon bisulphide also present in the gas, is partially absorbed by the ammonium polysulphide with formation of ammonium thiocarbonates, which under certain conditions undergo decomposition into ammonium thiocyanate.

Naphthalene.

Naphthalene occurs in large quantity in the volatile products given off from coal during distillation, but is almost completely removed during condensation and passes away with the tar. As, however, naphthalene has an appreciable vapour pressure at the ordinary temperature, the purified gas frequently contains small quantities, although the amount rarely exceeds from 15 grs. to 20 grs. per 100 cb. ft. Even this small quantity is frequently sufficient to cause serious trouble by its subsequent deposition in the solid state in the mains and services, both on the works and in the district of supply, and its estimation is therefore often a matter of importance.

No satisfactory simple method of estimating the amount present in the hot gas has been devised, owing to the difficulty of separating the tar-fog without simultaneously effecting a partial removal of the naphthalene still present as vapour in the gas, but for the cooled gas free from tar-fog, several methods are used, all of which depend on the fact that naphthalene combines with picric acid to form the crystalline picrate, $C_{10}H_8 \cdot C_6H_3N_3O_7$, which is practically insoluble in saturated picric acid solution, although it is partly dissociated into its constituents by water.

Colman and Smith[2] have introduced a slight modification of their original method[3] for the determination of naphthalene in coal gas, in which the gas is passed through a series of four wash-bottles, the

[1] *Annual Report on Alkali, etc., Works*, 1906, p. 461.
[2] *J. Gas Lighting*, 1918, 144, 231-232. [3] *J. Soc. Chem. Ind.*, 1900, 19, 128.

first—of glass throughout—containing a 10 per cent. solution of citric acid to retain any ammonia. The second contains 100 c.c. of $N/20$ picric acid and the third 50 c.c. of the same solution; the last is left empty to retain spray. It is important that the gas should not have access to india-rubber, prior to and during its passage through the train of wash-bottles, for a length of about 18 in. of india-rubber absorbs the whole of the naphthalene in gas containing 6 to 10 grs. per 100 cb. ft., when the latter passes at the rate of from 0·5 to 1 cb. ft. per hour.[1] The picric acid solution is standardised with $N/10$ sodium hydroxide solution, lacmoid or phenolphthalein being used as indicator. The gas (about 10 cb. ft.) is passed through the apparatus at a rate not exceeding 1 cb. ft. per hour, the volume being corrected to N.T.P. (generally 60° F. and 30 in. pressure). After passage of the gas, the contents of the third and fourth bottles of the train are washed into the second bottle, which is then closed with a tight-fitting rubber stopper fitted with glass stopcock or similar device. By means of a pump, the wash-bottle is evacuated until the precipitate rises to the surface. The stopcock is then closed and the contents heated to boiling by immersion in a bath with occasional shaking and then allowed to cool, the shaking being continued to prevent sublimation of the naphthalene into the upper part of the bottle. The whole of the naphthalene is thus converted into naphthalene picrate. The volume of the cold mixture is measured, the precipitate is filtered off through a dry filter paper, the first few cubic centimetres of filtrate being rejected, and 100 c.c. of the filtrate titrated with $N/10$ NaOH solution. If v c.c. is the difference between the volume of $N/10$ NaOH required to neutralise the total volume of $N/20$ picric acid originally taken and that required for the neutralisation of the total volume of picric acid solution after heating and filtering, then—

$$\text{grains of naphthalene per 100 cb. ft.} = \frac{19.75v}{\text{volume of gas passed}}.$$

A modified method, which is sometimes convenient, though rather less accurate, is to filter off at the pump the naphthalene picrate which separates after the heating process, wash once with a small quantity of water, then wash the precipitate from the filter paper into a flask, heat till all is dissolved and titrate the hot solution with $N/10$ alkali. The volume of alkali used should be identical with v above, and the quantity of naphthalene is calculated by the same equation. Slightly lower results are usually obtained in this manner.

Knublauch[2] has criticised the Colman-Smith method of naphthalene determination and states that all the naphthalene is not precipitated in

[1] *J. Gas Lighting*, 1900, **76**, 414.
[2] *J. Gasbeleucht.*, 1916, **49**, 525-540; *Gas Journal*, 1917, **137**, 64.

combined form, and that the use of a separate vessel for ammonia absorption renders the method unsuitable for use with warm gases. After very detailed investigations of the factors involved, he has devised two methods of determination, termed respectively the *difference* and the *direct* titration method. The difference method follows the lines of the Colman-Smith method already described, two vessels containing a 1 per cent. solution of picric acid being employed. The "direct titration method" is simple and applicable to warm gases, while no separate vessel is necessary for prior absorption of ammonia, cyanogen, phenols, etc. The first of two cylindrical wash-bottles contains 110 c.c. of a mixture of 40 c.c. of 1 per cent. picric acid solution, 40 c.c. of *N* sulphuric acid, and 30 c.c. of water. The second wash-bottle contains 25 c.c. of a 1 per cent. picric acid solution. In the absence of ammonia, 1 per cent. picric acid solution is used in both bottles and from 50 to 55 litres of coal gas are passed through the wash-bottles. When sulphuric acid is used in addition to picric acid, from 80 to 85 litres of gas are passed. Towards the end of the absorption, a little picrate is formed in the second vessel. The whole of the precipitate is transferred to a filter and washed with a 0·2 per cent. picric acid solution until free from sulphuric acid. The precipitate and filter paper are then transferred into the second cylinder and titrated with *N*/10 alkali, using phenolphthalein as indicator, 0·1 c.c. *N*/10 NaOH being allowed for the picric acid used in washing, and the naphthalene content is calculated from the titration result as described above.

Jorissen and Rutten[1] emphasise the fact that low results are obtained by the picrate method if the naphthalene picrate is washed with much water. They find further that when a saturated solution of picric acid containing also solid picric acid is employed, the naphthalene picrate is directly precipitated from the gas as undissociated picrate. They therefore recommend the following procedure:—

Two hundred and fifty c.c. of a saturated solution of picric acid is evaporated to about 150 c.c. and transferred, while hot, to two absorption bottles. The gas, previously freed from tar-fog, cyanogen, sulphuretted hydrogen, and ammonia, is passed through the bottles at the rate of about 1·5 cb. ft. per hour, until a fair quantity of picrate has been formed in the first bottle. The solution and precipitate are then washed into a flask, made up to 250 c.c., the closed flask heated to 40° for about half an hour, and shaken from time to time till all the picrate has dissolved. After cooling, the solution is filtered from the separated naphthalene picrate, and an aliquot portion of the filtrate titrated with *N*/10 alkali, the same volume of the original solution being also titrated. From the difference between the two titrations the amount of naphthalene is readily calculated, as on p. 316.

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 1179.

For general works' practice, it is satisfactory to absorb naphthalene in a solution of picric acid made by adding one volume of alcohol to four volumes of a saturated aqueous solution of picric acid.[1] No dissociation of naphthalene picrate then occurs, and heating *in vacuo* may be omitted.

Gair[2] uses acetic acid (sp. gr. 1·044) as an absorbent; this appears to be advantageous when testing hot gas. Naphthalene is precipitated from solution by addition of picric acid solution and is determined either volumetrically or gravimetrically.

Tar-fog.

The determination of tar-fog present at various points in the pipe-line system employed in coal-gas manufacture and storage is frequently of importance, and is conveniently made by the method proposed by Clayton and Skirrow.[3]

A long glass tube ¾ in. in external diameter is taken, a small hole ¼ in. in diameter blown near one end, and about 12 in. of the tube above this hole filled with loosely packed cotton wool, previously extracted with carbon bisulphide to remove fatty matter. The end of the tube near the small side hole is closed by a cork, and the tube inserted through a cork placed in a 1½ in. cock on the main conveying the gas, and so fixed that the small side hole faces the gas stream as nearly as possible two-thirds across the main, or one-third of the diameter from the side opposite to the cock through which it is inserted, this being the point of mean velocity of gas in the main. The whole of the filtering material should be within the main, so that it is kept at the same temperature as the gas to avoid condensation, and the gas is allowed to pass through the filter at such a rate that the gas velocity through the ¼ in. hole is greater than that of the gas in the main. It is only by observing these precautions that it is possible to obtain uniform results.

The gas, after passing through the filter, is purified by oxide of iron and measured in a meter, from 20 to 30 cb. ft. being passed. The tube is then removed from the main, the external surface wiped clean from tar, and the cotton wool containing the tar placed in a Soxhlet tube, and extracted with carbon bisulphide in a tared flask. The carbon bisulphide extract is evaporated off on the water-bath, dry air finally drawn through the flask for half a minute, and the flask again weighed. From the weight of oil and the volume of gas passed, the amount of tar-fog per 100 cb. ft. is readily calculated.

The free carbon in the tar remains in the cotton wool and some

[1] *Cf.* Somerville, *J. Soc. Chem. Ind.*, 1907, **26**, 1263.

[2] *Ibid.*, 1905, **24**, 1279; 1907, **26**, 1263.

[3] *J. Gas Lighting*, 1907, **98**, 660.

of the low-boiling constituents of the tar are evaporated with the carbon bisulphide, so that the results are low, but the figures obtained are fairly comparative and sufficiently exact for most practical purposes.

In Feld's method,[1] the gas drawn from the main, as already described, is passed through a weighed U-tube containing cotton wool. Before weighing, the latter is placed in a water-bath warmed to the temperature of the gas in the main, and the gas passed through it, after traversing two additional U-tubes placed in the same bath and filled with cotton wool (unweighed) and calcium chloride respectively until its weight is constant. The weighed tube is then connected directly with the tar-laden gas stream and a measured volume of gas passed. The tube is then re-connected to the outlet of the two U-tubes previously employed, and the gas again passed until the weight of the tar-absorption U-tube is constant; the increase of weight gives the amount of tar-fog in the volume of gas passed. Working in this manner, the moisture in the filtered tar is removed without simultaneous loss of tar vapours, as the gas employed is always saturated with tar vapours at the temperature of the gas main.

Oxides of Nitrogen.

The determination of oxides of nitrogen is of importance more especially in ammonia oxidation plants. In the absence of ammonia, nitric oxide and nitrogen peroxide are determined by absorption in standard alkali and titration of the excess of alkali with or without addition of hydrogen peroxide. Owing to the difficulty of absorbing nitric oxide by water or alkali, a large excess of peroxide should be used to ensure oxidation to peroxide.

In the gas leaving the catalyst of an ammonia oxidation plant, unoxidised ammonia is present along with the oxides of nitrogen. The use of hydrogen peroxide or other oxidising agent in this case needs special consideration, as hydrogen peroxide and ozone oxidise ammonia to ammonium nitrite. Fox[2] suggests the following procedure for the analysis of the mixture. The gas is mixed with a measured volume of oxygen sufficient to oxidise the nitric oxide, and is then passed through two absorption vessels. The first contains standard alkali only, and absorbs a portion of the nitrogen peroxide and all the ammonia unless this is present to an abnormal extent. The second contains standard alkali and hydrogen peroxide to about 1 per cent. concentration, to complete the absorption of nitrogen peroxide. Ammonia is determined by oxidation with sodium hypobromite, and nitrogen peroxide by separate titrations of the two absorbing solutions. The residual gas is measured in an aspirator and allowance made for the

[1] *J. Gasbeleucht.*, 1911, 54, 33.

[2] *J. Ind. Eng. Chem.*, 1917, 9, 737.

volume of oxygen added, the water vapour condensed from the gas in the first absorption vessel, and the small volume of oxygen evolved from the hydrogen peroxide. A simple formula is deduced from the results for the ratio of nitric oxide to ammonia. Different methods offering possibilities for the development of rapid works control have been devised by Taylor and Davis,[1] and by Gaillard[2] (see p. 487).

Nitrous oxide may be determined by combustion with either hydrogen[3] or carbon monoxide[4] in the Drehschmidt platinum capillary heated to bright redness (see p. 257). The use of carbon monoxide is preferable, as under certain conditions ammonia may be formed when hydrogen is used.

Sulphur Dioxide.

Sulphur dioxide may be determined by titration as described on pp. 393-400.

Sodium hydroxide is often employed for the determination of total acid gases, and the results obtained combined with that afforded by iodine solution make it possible to determine SO_2 and SO_3 separately. When the test is prolonged, oxidation of the sodium sulphite formed occurs, and this was shown by Titoff[5] tobe due to minute traces of catalysts, and to be prevented by employing a negative catalyst; Haller[6] recommends the use of glycerol for this purpose.

Hydrogen Phosphide.

The determination of traces of this gas in technical acetylene is of great importance. Hydrogen phosphide, together with sulphur or silicon compounds, can be detected by bubbling the gas through an acid solution of mercuric chloride, or by causing the gas to impinge upon a black filter paper soaked with mercuric chloride and moistened with 10 per cent. hydrochloric acid; a white stain results if compounds of phosphorus, sulphur, or silicon are present.

The quantitative determination depends upon the oxidation of hydrogen phosphide to phosphoric anhydride. Lunge and Cedercreutz[7] pass a known volume of acetylene through a ten-bulb tube containing a 2 to 3 per cent. solution of sodium hypochlorite. The liquid is washed into a graduated flask and phosphoric acid estimated in one half as magnesium pyrophosphate. The remaining half is employed for determining sulphur as barium sulphate. There is risk of explosion when passing acetylene through the hypochlorite solution.

[1] *J. Ind. Eng. Chem.*, 1917, 9, 1106. [2] *Ibid.*, 1919, 11, 745.
[3] Knorre and Arndt, *Ber.*, 1889, 21, 2136.
[4] Treadwell and Hall, *Anal. Chem.*, 5th ed., 1919, 2, 802.
[5] *Z. physik. Chem.*, 1903, 45, 641. [6] *J. Soc. Chem. Ind.*, 1919, 38, 52 T.
[7] *Z. angew. Chem.*, 1897, 10, 651.

Dennis and O'Brien[1] modify this method by producing the acetylene from calcium carbide without marked rise of temperature in a small Kipp's apparatus by means of a saturated solution of sodium chloride, and by employing for absorption a Friedrich's gas-washing bottle, modified so as to permit easy rinsing with water at the end of the passage of gas. Methods in which the acetylene is burnt, and the phosphoric anhydride determined in the products of combustion, have been devised by Eitner and Keppeler,[2] and by Gatehouse.[3] The latter burns the gas at the rate of about 10 litres per hour in an ordinary burner under a bell jar. The products of combustion pass through a drying-tower and a long condensing tube down which a little water trickles. The apparatus, at the end of the test, is cooled, washed out with water, and the phosphoric acid in the condensate and washings titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator.

AUTOMATIC GAS ANALYSIS

Various forms of apparatus, which automatically determine and record the percentage of a constituent gas in a mixture, are available, more especially for the determination of carbon dioxide.

In the simplest forms a soda-lime absorbing vessel is placed between two synchronously running gas meters, and the CO_2 percentage read off from the difference of the volume of the gas before and after absorption of CO_2 as in the *Bi-Meter CO_2 Recorder*.[4] To reduce the error due to variations in temperature in the gas in the two meters, the gas passes through a water cooler prior to entering the individual meters.

Simmance's Combustion Recorder. The "S. A. W." combustion recorder[5] is shown diagrammatically in Fig. 167. The apparatus is operated as follows. Water passing through the injector A in the water supply, causes a continuous stream of gas to be drawn out of the pipe-line from the flues B; this is seen bubbling through the water in the tell-tale chamber C. After passing through the injector the water flows into a tank E fitted with a syphon pipe F, which empties the tank when full.

As the syphon discharges the water more rapidly than it flows in, the tank is periodically filled and emptied. Standing inside the syphon tank is a metal bell, G, having an inlet pipe, H, communicating with the flue pipe through a simple non-return liquid seal, J, and an outlet pipe

[1] *J. Ind. Eng. Chem.*, 1912, 4, 834.
[2] *J. Gasbeleucht.*, 1901, 44, 548.
[3] *Acetylene*, 1908, 5, 167; 1909, 6, 58.
[4] Made by the Cambridge and Paul Scientific Instrument Co., Ltd., Cambridge, England.
[5] Supplied by Messrs Alexander Wright & Co., Ltd., Westminster.

K, opening to air through another liquid seal, L. Within the bell is a smaller gas chamber, M, open at the bottom, with an outlet pipe at the top which is led down into the tank containing the potash solution, N. As the surrounding water in the syphon tank falls, so a sample of gas from the continuous stream is drawn into the bell, and as the water

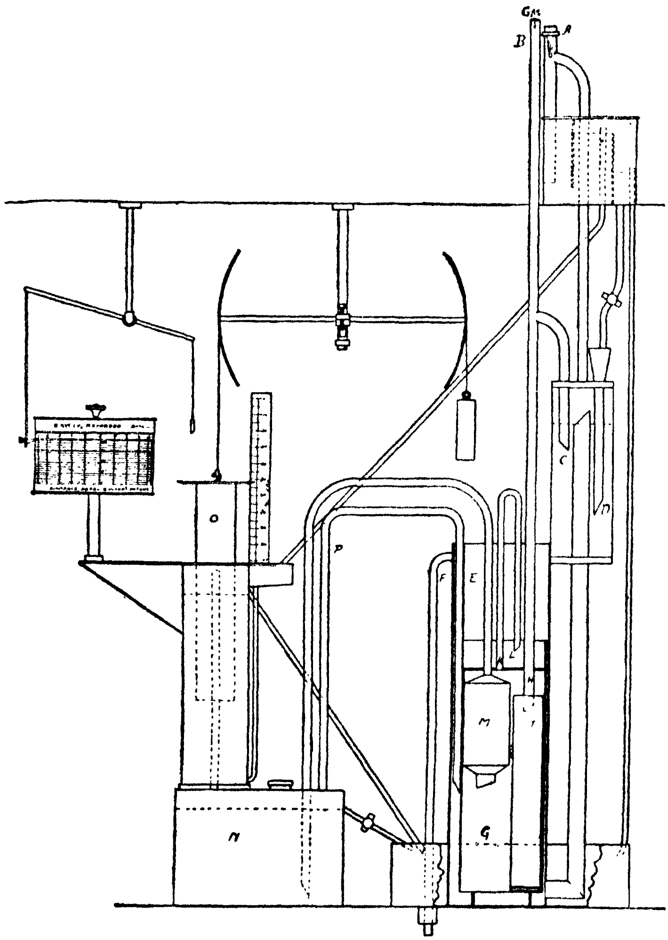

FIG. 167.

rises the bulk of the sample is discharged through the outlet seal, while the remainder in the smaller gas-chamber is forced through the potash solution, and rises under the measuring bell, O, the bent pipe of which has been meanwhile closed by the water in the syphon tank. The quantity of gas trapped in the inner bell is just sufficient to raise the moving bell over the scale of 100 divisions when no carbon dioxide is present and absorbed in the potash solution. If the sample of gas

drawn in contains carbon dioxide, the bell is not raised so high, the height being a direct indication of the percentage volume of the carbon dioxide contained in the sample.

The height is recorded by a pen mechanism and an analysis completed about every three minutes. The ends of the pen markings form a continuous curve.

The apparatus and its mode of operation is slightly modified when employed for recording the percentage of carbon dioxide in illuminating gas. The apparatus is also applicable, with slight modification, to the determination and recording of the percentage of carbon monoxide in coal gas, producer gas, water gas, etc. For this purpose the entering gas is aspirated through a train of reagents, whereby carbon dioxide and ethylene are first removed from the gas and the carbon monoxide subsequently oxidised to carbon dioxide.

Other forms of carbon dioxide recorders of this chemical type are supplied by the "Sarco" Engineering Co., London, and the W. R. Patents, Ltd., Leeds. These, together with the Arndt and the Webster carbon dioxide recorders, the Levy and Simmance carbon monoxide and the Edwards sulphuretted hydrogen recorders, are described in *Gas Works Recorders*, by L. Levy, London, 1922.

The Katharometer.—The katharometer, initially designed by G. A. Shakespeare[1] for indicating the presence of small quantities of hydrogen in air, has been developed by the Cambridge and Paul Scientific Instrument Co., for recording the percentage of carbon dioxide in flue and other gases.

The instrument utilises the principle that the heat loss from a fine heated wire surrounded by gas within a small enclosure is conditioned by the thermal conductivity of the gas in the enclosure. The instrument contains two identical spirals of platinum wire, enclosed in two separate cells in a metal block (Fig. 168), each of the spirals being connected to form one arm of a balanced Wheatstone bridge circuit as in Fig. 169, the other two arms being coils of manganin wire. If an electric current flows in the circuit, the spirals become heated

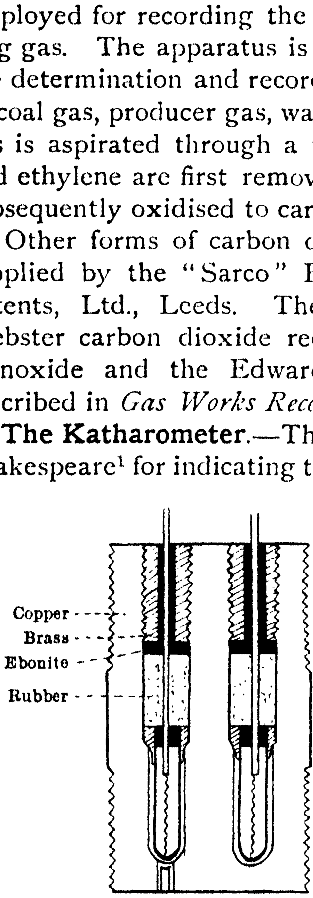

FIG. 168.

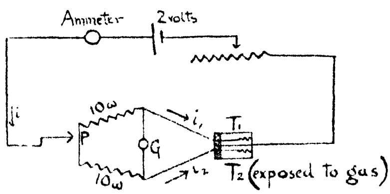

FIG. 169.

[1] *Roy. Soc. Proc.*, 1920, **97**, 273; *Proc. Phys. Soc.*, 1921, **33**, 165.

and will lose heat to the walls of the enclosures. If the respective enclosures contain gases of different thermal conductivities, the spirals will cool at different rates, and the difference of temperature of the two wires will cause a deflection of the galvanometer, which is dependent on the difference in thermal conductivity of the two gases. If, therefore, one of the enclosures contains a pure gas and the other a mixture of two gases, the deflection will be a measure of the amount of the second gas present, and the galvanometer scale can be calibrated so as to indicate directly the composition of the mixture. Either an indicating or recording galvanometer may be employed. The

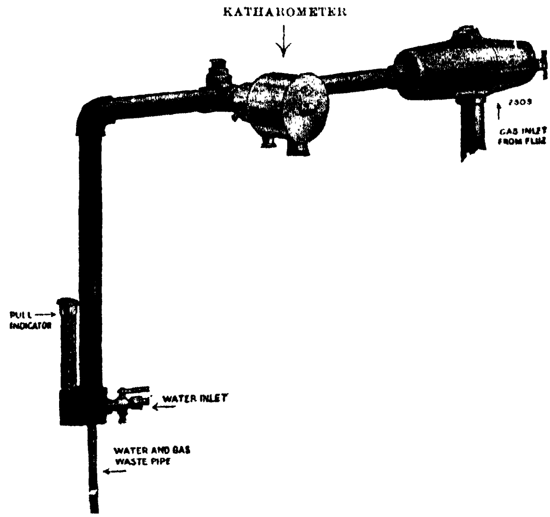

Fig. 170.

arrangement thus resembles that of the platinum resistance thermometer (p. 152).

The thermal conductivity of hydrogen at ordinary temperatures is about five times that of any other gas with the exception of helium, the thermal conductivity of which is slightly larger. The katharometer is therefore extremely suitable for the determination of the purity of hydrogen, or the admixture of hydrogen with air or other gases. The chief limitation of the method is that it can give no qualitative information, and can only give quantitative results in certain special cases. It is almost impossible to deal with very complicated mixtures of gases. Moreover, the sensitiveness depends slightly on temperature and very largely on the current in the bridge, which must therefore be adjusted about once a day.

The instrument has found application in detecting dangerous mixtures in the neighbourhood of hydrogen generating plants, in the

determination of leakage of hydrogen and helium through balloon fabrics, etc., and the analysis of nitrogen-hydrogen mixtures employed in ammonia synthesis. Nitrous oxide, carbon dioxide, and methane in air are mixtures which lend themselves readily to analysis by the method. The analysis of producer gas, blue water gas, coke oven and blast furnace gases is not at present possible by the method. The instrument has, however, been satisfactorily applied to recording carbon dioxide in flue gases. Of the gases present, nitrogen, oxygen, and carbon monoxide (in certain cases) have nearly the same conductivity. The quantity of hydrogen and methane is extremely small, and the gas is always saturated with water vapour at the temperature of the instrument.

For measuring the percentage of carbon dioxide in flue gases, the katharometer is mounted in a head carrying the two manganin bridge coils, and a series coil in the galvanometer circuit which makes all katharometers interchangeable. Flue gases are aspirated over one of the platinum spirals by inserting the head in the flow system, as shown in Fig. 170, the gases being previously filtered through wood wool, linen, and glass wool. Four-way leads are taken from the katharometer to the indicator or recorder situated at any distance. A single indicator may be employed with a number of katharometers, convenient switches being mounted on a panel near the indicator.

Other Forms of Gas-Analysis Apparatus operated Electrically.

Various devices for analysing gases automatically, and more especially for indicating the presence of a definite maximum amount of one combustible constituent, have been developed by Weaver and Weibel, and others.[1]

These depend upon the combustion at the surface of an electrically heated platinum wire of the gas contained in the surrounding atmosphere. This combustion takes place at a temperature much below the normal ignition temperature of the gas. The resulting rise in temperature of the wire depends upon the quantity of combustible gas present. The measurement of temperature is effected in various ways. Thus the compensated bridge indicator (p. 153) consisting of a Wheatstone bridge of four platinum wires, two of which on opposite sides of the bridge are rendered inactive by a thin coating of inactive material, may be used in the manner described above. A voltmeter with scale graduated to show the percentage of the combustible gas (*e.g.*, hydrogen in electrolytic oxygen, carbon monoxide in air about producers, etc.) is connected across the bridge, and serves to indicate at all times the percentage of the gas in question present.

[1] See *Bureau of Standards, Scientific Papers*, 1919-20, 15, 47.

A contact-making attachment causes an alarm to ring when the amount of gas reaches the limit for which the contact has been set.

A glowing-wire indicator consists of two short lengths of fine platinum wire, the currents through which are supplied by a dry battery and controlled by two small rheostats. One wire is active, the other inactive. By adjusting the rheostats, the two wires may be made to glow with the same intensity. One rheostat determines the ratio of the currents in the wires, and can be graduated so as to indicate the percentage of the combustible constituent directly. The device is practically independent of the illumination at the place of use and independent of the voltage of the battery used. The glowing-wire indicator is suitable for use in detecting leaks in gas mains, and in examining spaces in which the presence of a dangerous amount of combustible gas is suspected.

The bimetallic detector, intended only to actuate an alarm or other device when the amount of combustible gas attains the limit for which the alarm is set, consists of two bimetallic strips, with one end of each rigidly fixed to an insulating support. A millimetre or two below the strips are stretched platinum wires, one active, the other inactive, which serve to heat the bimetallic strips. When equally heated the strips bend equally, but when unequally heated, they indicate by a relative movement of their free ends the difference in temperature. The platinum wires are connected in series to any convenient source of electric current, direct or alternating. The free ends of the bimetallic strips bear contact points which, when the strips come together, short-circuit the platinum wires through an alarm. One of the contacts is adjustable, permitting the instrument to be set for various percentages of combustible gas. The instrument is readily adjustable to sound the alarm at less than 0·1 per cent. of hydrogen. A somewhat similar device has been employed by Alderson and Holmes.[1] For an automatic method of determining carbon monoxide, see p. 323.

LITERATURE

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[1] B. P., No. 24371, of 1909.

FUEL ANALYSIS

By G. NEVILL HUNTLY, B.Sc., A.R.C.S., F.I.C., Consulting Chemist, London

ANALYSES, from the fuel standpoint, may be required of wood, peat, lignite, coal, and their products of carbonisation, wood charcoal, coke, gas, and tar products. To these must be added petroleum products, and less frequently vegetable oils.

Wood, wood charcoal, and peat need hardly be considered, as determinations of moisture and ash usually give all the information required.

Sampling.—Unless the portion analysed is truly representative of the bulk, an accurate analysis is worthless. Moreover, if any doubt arises, the analysis of the laboratory sample can be repeated, but it is usually impossible to get another sample from bulk. The sampling must be carried out according to a properly worked-out plan, and if the price paid for the fuel depends on the analysis, the method of sampling should be a part of the contract. With coal, difficulties of sampling are caused by the presence of lumps of shale, slate, bone, or pyrites and variations in the ash and moisture of the coal substance. Coal is far from being the homogeneous substance it appears to be externally—a fact not always appreciated by engineers or other coal users: hence the problem of coal sampling should be considered as identical with that of ore sampling. As showing the variations in apparently homogeneous coal, the following examples are of interest. In a piece of Deister coal weighing 5 kilograms, Fischer found the ash to vary from 4 per cent. to 31 per cent. in different portions of the sample. In twenty-four samples from the Unser Fritz mine, the ash varied only between the limits of 1·1 per cent. and 7·8 per cent. Eight samples of coal from a Leicestershire mine showed ash varying between 8·4 and 16·6 per cent., and fifteen samples of anthracite from another mine had ash contents between the limits 3 and 41 per cent. In the two last series the samples were clean coal and free from bone and slate. The general problem of sampling has already been dealt with on

pp. 4-12. For fuller details of coal sampling, reference may be made to the Report of the Committee on Steam Engine and Boiler Trials (Institution of Civil Engineers, 1914), and to Bulletin 116 of the U.S. Bureau of Mines ("Methods of Sampling Delivered Coal," by George S. Pope, Washington, 1918). In a valuable paper on coal sampling, E. G. Bailey[1] emphasises the necessity of keeping a proper relation between the size of the largest lump present and the weight of the sample containing it. He gives the following table, based on an extensive series of experiments:—

Size to which Coal should be broken before quartering or dividing Samples of Various Weights.

Weight of sample to be divided. Lbs.	Maximum size of lumps. Ins.	Weight of sample to be divided. Lbs.	Maximum size of lumps. Ins.
7500	2	40	2 mesh
3800	1·5	5	4 mesh
1200	1	0·5	8 mesh
460	0·75	0·25	10 mesh
180	0·5		

Washed coal, or any coal showing visible moisture, cannot be reduced to a 5-lb. laboratory sample without serious error. Some experiments carried out by the writer showed that this error may amount to as much as 5 per cent., and other workers have also found errors of the same order. This error can be minimised by dividing rapidly down (with crushing if necessary) to a 100 or 200 lb. sample, and air-drying this on a metal tray weighed on an ordinary steel-yard weighing machine. (For details see Report of I.C.E. Committee above quoted.)

Although many text-books on fuel, and original papers on boiler trial fuel sampling, etc., give ample details of the methods of sampling, data from which the accuracy of such sampling can be checked are very infrequently given, and hence some examples drawn from actual practice may be of interest. From a lighter containing 100 tons of Welsh coal (large coal with about 30 per cent. of slack, air dry) two bulk samples of about 2 tons each were taken during unloading by withdrawing a shovelful from each skip, care being taken to keep the right proportion of large coal and slack. The first heap, B, was reduced to a 10-lb. sample by crushing and quartering by hand in the usual manner. The other heap, A, was treated similarly, but portions of the rejected halves were worked down to small bulk separately, using a

[1] *J. Ind. Eng. Chem.*, 1909, 1, 161-178.

riffle sampler. These samples were labelled A_1, A_2, A_3, etc. The results were as follows:—

No.	B.T.U. per lb.	Moisture. Per cent.	Ash. Per cent.
A_1	15,000	1·1	5·5
A_2	14,680	1·1	6·0
A_3	14,750	0·9	6·7
A_4	15,040	1·5	5·3
B	14,900	1·3	7·0
Mean . . .	14,874	1·2	6·1

Error expressed as deviation from the mean:—

	Per cent.	Per cent.	Per cent.
Maximum . . .	+1·1	+0·3	+0·9
Minimum . . .	−1·3	−0·3	−0·6
Average	±0·8	±0·2	±0·8

Duplicate samples from bulk taken by the writer during numerous boiler trials have given differences of the same order, about 1 per cent. Washed slack, with a preliminary air-drying of a 200-lb. sample, gives smaller differences, 0·3 to 0·4 per cent. On the other hand, small 5-lb. samples obtained directly from washed slacks, without air-drying on the large sample, show differences up to 5 per cent. Another example of coal sampling from a barge is given below. One sample was formed by taking a shovelful from the 50th, 150th, 250th grab, and so on; the other started with the 100th grab, so that the two sets overlapped right through the cargo. Each of these was independently reduced to small bulk in the usual way. The figures obtained were:—

	No. 1 Sample.	No. 2 Sample.
Moisture . . .	10·4 per cent.	10·0 per cent.
Ash	9·6 ,,	9·2 ,,
Calorific value . .	12,900	13,020

With reasonable care and experience it is clear that coal can be sampled *when being shifted* with an accuracy of 1 per cent., and in special cases, such as washed screened coal, to between 0·3 per cent. and 0·5 per cent.

The whole of the laboratory sample is air-dried to constant weight in a small weighed tray (the original container being weighed with it if there is visible moisture), then rapidly reduced to powder in a coffee mill, or by other mechanical means, and finally powdered to at least 100 mesh in a small closed ball mill. Grinding in a mortar, or in certain forms of disc grinders, leads to a loss of moisture, owing to the local rise of temperature due to friction. In coke sampling the hardness must be borne in mind and care taken to avoid contamination from metallic iron derived from the grinding apparatus.

Moisture.—For washed or visibly wet coals the preliminary air-drying on at least 100 lb. described above is essential, and the figure

obtained should accompany the small laboratory sample. The whole of the latter is air-dried to constant weight in the laboratory before reduction to powder, and all the laboratory determinations are carried out with the air-dried material and the results calculated back to the original coal.

One g. is weighed into a shallow weighing bottle (depth 22 mm., diameter 28 mm.) and heated to 105° to 107° in a constant temperature ventilated oven heated by toluene or glycerol, cooled in a desiccator over strong sulphuric acid, and weighed stoppered. Dry coal-dust is very hygroscopic, and the use of open crucibles or dishes as containing-vessels or of an inefficient desiccator gives low moisture figures. A good alternative method, if a suitable air-pump is available, is to dry for forty-eight hours in a vacuum of about 1 mm. of mercury over concentrated sulphuric acid at the ordinary temperature. (The Report of the Sub-committee of the Eighth International Congress of Applied Chemistry on the Determination of Moisture, 1912, contains a large amount of information on the determination of moisture in coal and a comparison of various methods. See also an abstract of this report with some additional data by G. N. Huntly and J. H. Coste.[1])

A third method, useful for the estimation of moisture in coals liable to oxidation when heated in air, is based on the distillation of the coal with a liquid not miscible with water, such as benzene, xylene, or petroleum. This method was used by Marcusson for the estimation of water in oils, fats, soaps, and resins, and was applied to coal by Schlapfer.[2]

Fifty to 100 g. of the fuel, according to the water content, is brought into a 500 c.c. flask and 200 c.c. of xylene added. The flask is connected with a vertical condenser by a tube of about 1 cm. diameter and the distillate received in a measuring tube of the form shown in Fig. 171. The flask is cautiously heated until the liquid is in a state of quiet ebullition: after 30 c.c. of distillate has been collected, the distillation can be conducted more rapidly, about 150 c.c. being collected in thirty minutes. The collection of the water under the xylene layer is facilitated by placing the tube in warm water, and bringing down any drops adhering to the side with a wire. Careful cleaning with steam and chromic acid solution after each determination reduces the tendency for drops to hang on the sides. The tube must be calibrated, but other corrections for the shape of the meniscus, solubility of the water in the xylene, and losses during distillation are best made by running a distillation on weighed quantities of water.

An improvement on this method has been recently described by

[1] *J. Soc. Chem. Ind.*, 1913, **32**, 62.

[2] *Z. angew. Chem.*, 1914, **27**, 52. A bibliography of the extensive literature on this method is given in *J. Ind. Eng. Chem.*, 1920, **12**, 490.

E. W. Dean and D. D. Stark.[1] The special point is the shape of the graduated receiver (Fig. 172). The condensed water is collected in the closed end, and the excess of hydrocarbon flows back into the distilling flask, which is round-bottomed and of 500 c.c. capacity. A mixture of

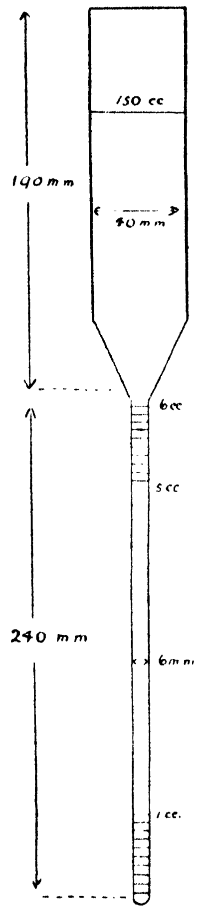

FIG. 171.

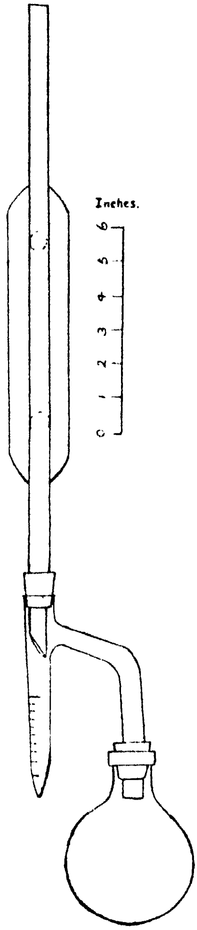

FIG. 172.

80 per cent. of commercial xylene and 20 per cent. of commercial "90 per cent. benzol" is recommended by the authors. Results with measured amounts of water agreed within 0·1 c.c., which is apparently the normal experimental error. For substances containing small percentages of water a larger distillation flask and correspondingly larger quantities of material will give higher accuracy. When applied to coals, this method can be used where there is a tendency to oxidise in the oven, and the use of 50 or 100 g. samples obviously gives a

[1] *J. Ind. Eng. Chem.*, 1920, 12, 488.

better average result than in methods working on 1 g. For oils the method is in general use, and it is specially suitable for tar oils or emulsions containing large percentages of water, in which direct distillation gives rise to unpleasant bumping.

Ash.—For coal, coke, lignite, or other solid fuel, a 1 g. portion is heated in a flat-bottomed porcelain dish, platinum dish, or tray, in a gas or electric muffle. The heating must be gradual and the dish should be covered until the coking stage is passed, as particles are liable to be thrown out of the dish owing to decrepitation. The cover is removed and the carbon burnt off at as low a temperature as possible, about 750°-800°. The joint Committee of the American Society for Testing Materials and the American Chemical Society recommend a muffle temperature of 700° to 750°.[1]

The ashing is more rapid when the fuel is spread out in a thin layer in this manner than when a crucible is employed, and no stirring is required. After cooling and weighing, the ash is treated with a little alcohol, when any unburnt particles will be visible. The alcohol is evaporated on the water-bath, thus causing the ash to adhere to the dish, which is reheated in the muffle for thirty minutes and again weighed. The process is repeated until the variation in weight between two successive ignitions is 0·0005 g. or less, and no unburnt particles show on treatment with alcohol.

G. Lunge determines the ash in a crucible. A circular hole is cut in a piece of asbestos board or quartz plate and the crucible is placed in this as shown in Fig. 173; the flame thus comes in contact with the lower part of the crucible only, and the fuel itself is in free contact with air. The temperature should be kept as low as possible consistent with combustion, and the contents of the crucible frequently stirred.

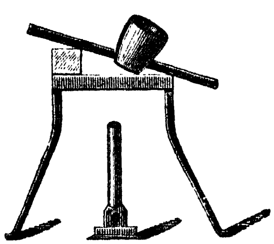

Fig. 173.

During the incineration of the coal various chemical changes other than the removal of combustible matter may take place—removal of carbon dioxide from carbonates, oxidation of iron pyrites to ferric oxide, formation of silicates, etc.—and hence the weight of the ash will depend to some extent on the temperature of ignition. If the ash content of a coal is required for controlling deliveries under a contract, the incineration temperature should be given in the specification, although if the carbon is burnt off at the lowest possible temperature the results are usually consistent. A suitable type of gas muffle is shown in Fig. 174, and an electric muffle in Fig. 175: the latter permits

[1] *J. Ind. Eng. Chem.*, 1917, **9**, 100. See also F. Weisser, *Chem. Zeit.*, 1914, **38**, 1264, 1289, and *J. Soc. Chem. Ind.*, 1915, **34**, 130; and F. M. Stanton and A. C. Fieldner, "Methods of Analysing Coal and Coke," Bureau of Mines Technical Paper 8, Washington, 1912.

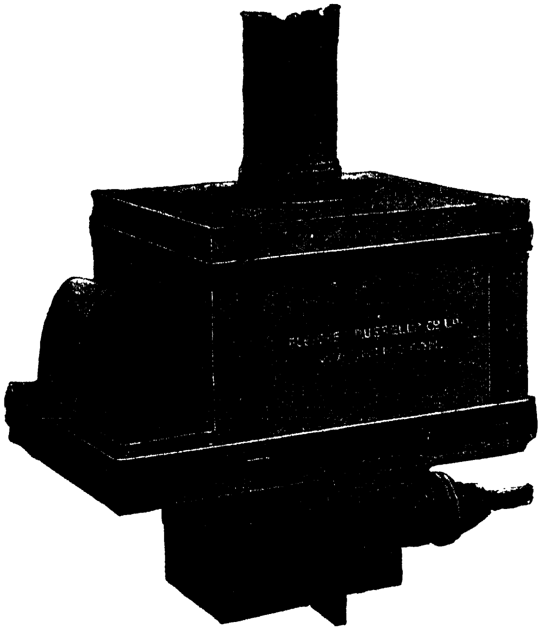

FIG. 174.

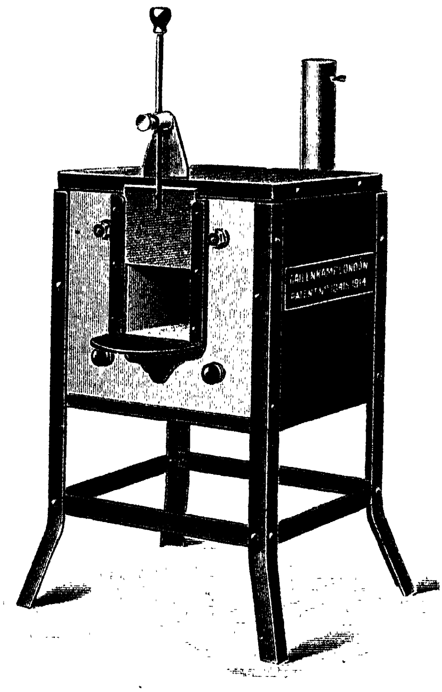

FIG. 175.

a very exact temperature control. After weighing, the ash may be kept for analysis.

The determination of ash in oil requires some special precautions. From 25 to 50 g. of oil is weighed out into a platinum dish and heated very gently, preferably over a luminous Argand burner turned low, so that the oil gradually evaporates without catching fire. When no more vapour is visible, the dish is covered and the residue gently raised to the coking temperature. On removing the cover, the residue should smoulder away without flame; the final ignition is most conveniently done in the muffle. The ash from oil, and from some bitumens, is light and pulverulent and may readily be lost through the draught caused by carelessly opening the desiccator in which the dish has been cooled. If the oil is allowed to burn at any stage of the incineration, the draught produced by the flame is usually sufficient to carry away the greater part of the ash.

Volatile Matter and Fixed Carbon.—The amount of coke left after ignition of the coal in a closed crucible, minus the ash, is known as the *fixed carbon*, and the loss, after deducting moisture, is the *volatile matter.*

The determination of volatile matter is essentially empirical, and the results depend on the experimental conditions—*e.g.*, weight of sample taken, weight and material of the crucible, temperature and period of ignition. The different methods proposed and in use before 1909 were investigated and compared by E. J. Constam, and his results and conclusions given in a paper before the International Congress of Applied Chemistry in London, in 1909. With slight modification, the method proposed by the American Committee on Coal Analysis was then adopted as the international method. This is as follows:—1 g. of the fresh undried powdered coal is heated for seven minutes over the full flame of a Bunsen burner in a *polished* platinum crucible weighing from 20 to 30 g., and provided with a tightly fitting (capsule shaped) cover. The bottom of the crucible, which is supported on a platinum triangle, should be from 6 to 8 cm. above the top of the burner. The flame when burning free should be 20 cm. high, and care should be taken to protect it from draughts during the determination. The under surface of the cover should remain coated with carbon, but the upper surface should always keep free from it. Analyses for arbitration purposes made in different places by this method on the same sample show differences for the most part of less than 1 per cent. in the yield of coke, and only rarely as much as 2 per cent. In the case of lignites or coals with very high volatile matter, the seven minutes full heating is preceded by a preliminary heating for from four to five minutes over a low flame to avoid mechanical losses, and it is sometimes necessary to use a coarser powder to avoid decrepitation. Later refinements include

working at a fixed temperature in an electric muffle (925°), but these have not at present been generally accepted.[1]

Hence, in a proximate analysis of coal, the moisture, ash, and ash plus free carbon are experimentally determined. The fixed carbon is the coke residue obtained by the above method less the separately determined ash. The volatile matter is 100 − (fixed carbon + ash + moisture), or 100 − (moisture + coke determined as above). For purposes of classification the volatile matter is calculated to the basis of dry ash-free coal.

Sulphur.—Sulphur occurs in coal partly as organic compounds and partly in inorganic combination. These have been further subdivided; the inorganic into pyritic (or marcasitic) sulphur and sulphate sulphur, the organic into resinic and humic sulphur.[2] A distinction has also been made between total sulphur and "volatile sulphur," but the definition of the latter term is too vague to be of much practical service. The sulphur left in the ash after burning a sample in a boat in a combustion tube in a current of air or oxygen is always higher than that found in the ash from a combustion in compressed oxygen, as in the calorimetric bomb, and the percentage of sulphur in the ash of the same coal burnt under a boiler may give yet a third figure. The term volatile sulphur is also sometimes taken to represent the amount contained in the volatile matter driven off during dry distillation, and this can be calculated from the sulphur percentages in the coal and in the residual coke.

The estimation of total sulphur in any solid or liquid fuel is best carried out by combustion in a bomb (see p. 347) under a pressure of 30 to 40 atmospheres, the higher pressure being used if the sulphur percentage is high. The quantity taken for combustion depends on the amount of sulphur in the fuel and on the capacity of the bomb. The bombs in use range from 180 c.c. to 500 c.c. capacity, and the larger the capacity the less the difficulty in securing complete combustion. For coal, 1 g. is a suitable amount; 10 c.c. of distilled water are placed in the bomb before filling at 30 atmospheres pressure. The sulphuric acid formed is partly present in the form of fog, and if the pressure is released too soon after firing, low results will be obtained. Hence at least twenty minutes should be allowed between firing and releasing the pressure. Care should be taken that the washer, if of lead, is kept clean and free from incrustation. After opening up, the contents of the bomb are washed out into a beaker, 5 c.c. of a saturated solution of sodium bicarbonate added, and the liquid boiled down to small bulk to decompose any lead sulphate arising from the washer, and the precipitate filtered and washed. Even in the absence of a lead washer

[1] If the temperature is fixed (925° on the bottom of the covered crucible inside), the method of heating may be varied. A muffle furnace or simple form of tube furnace is convenient.

[2] A. R. Powell and S. W. Parr, "A Study of the Forms in which Sulphur occurs in Coal," University of Illinois Bulletin No. 116, 1919.

a filtration is always necessary to remove any particles of enamel which may have been detached. The washings are acidified with hydrochloric acid, and the sulphate precipitated in the usual manner with barium chloride. Some bombs have been sold the enamel of which contained a soluble sulphate; the washings from such instruments after burning a material free from sulphur show appreciable amounts of sulphate, even after prolonged use. A few combustions of benzoic acid (which can easily be obtained practically free from sulphur) and analysis of the bomb washings will show whether the bomb is suitable for sulphur determinations. The residue in the platinum capsule may contain sulphur corresponding to 0·05 per cent. (or less) of the total sulphur in the coal. It should be fused with a little sodium carbonate and the solution added to the washings.

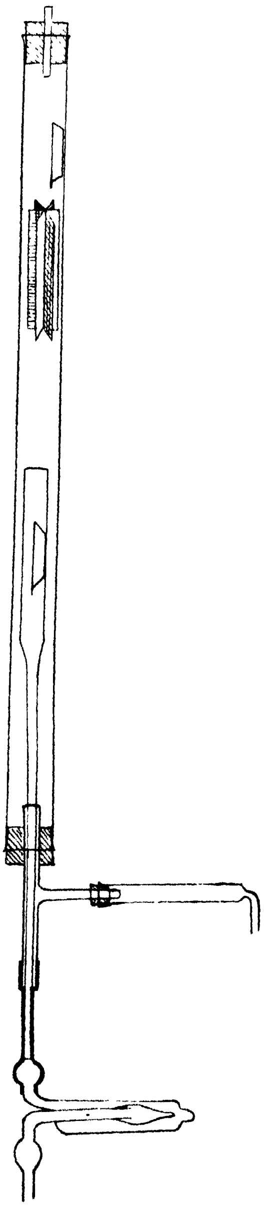

FIG. 176.

For oil, 0·7 g. is a suitable amount if the sulphur is 1 per cent. or under; for oils high in sulphur such a quantity of oil should be taken as to give not more than 0·15 g. barium sulphate; for oils very low in sulphur, several portions of 0·7 g. should be burnt and the combined washings analysed. In such cases, some blank combustions of pure benzoic acid should precede the actual determination. Duplicates should agree within 0·005 per cent. for low sulphur oils.

If a bomb is not available, combustion in a boat in a tube of hard glass or fused silica by the Dennstedt method (Fig. 176) is accurate and is applicable to both solid and liquid fuels, although with oils care and experience are required to prevent back explosions. Platinised quartz or the Dennstedt stars may be used as the catalyst. Oxygen purified in the usual way can be led into the combustion tube over the oil in the boat, or, independently, into the tube without passing over the oil. The combustion can thus be hastened or slowed down at will, an important advantage in dealing with oil. For petrols, the boat cannot be used and the liquid must be weighed in a small U-tube joined up to the

front end of the tube. The lamp method is more convenient for petrol. In the presence of the platinum catalyst the sulphur is wholly oxidised to the trioxide which can be caught by attaching one or more U-tubes filled with glass beads and moistened with decinormal sodium carbonate. After the combustion is completed, the combustion tube is cooled and washed out, since traces of sulphuric acid are retained by the glass, and the excess of sodium carbonate titrated with decinormal hydrochloric acid. Alternatively, the washings may be acidified and precipitated with barium chloride in the usual manner. In the case of coal or solid fuel, the ash in the boat must be fused with a little sodium carbonate, etc., to recover the traces of sulphates remaining in the ash. It has been stated that when a quartz tube is employed no sulphuric acid is retained and the washing out is unnecessary.

For coal, Eschka's[1] method is in common use. About 1 g. of the finely powdered sample is mixed in a platinum crucible with 3 g. of a mixture of two parts of well calcined magnesia and one part of anhydrous sodium carbonate. The open crucible is placed in a hole cut through an asbestos board (Fig. 173), and is heated in such a way that the lower half only of the crucible attains a red heat. Heating is continued for about an hour, the mixture being frequently stirred with a platinum wire. As soon as the grey colour of the mixture has given place to a uniform yellowish, reddish, or brownish tint, the heating may be considered to be finished. After cooling the crucible is placed in a beaker and covered with water; this is gradually heated to boiling, and extraction is completed by successive additions of water. Bromine water is then added until the liquid becomes slightly yellow and the solution warmed to effect the oxidation of any sulphides present, or after warming with bromine water the whole may be dissolved up with hydrochloric acid. The whole is then filtered, the filtrate acidified with hydrochloric acid, and barium chloride added to the boiling solution. From the amount of barium sulphate obtained the sulphur is calculated. The time required may be shortened by making the solution upto a known volume and filtering an aliquot portion through a dry filter, and if an electric muffle is available, the heating may be carried out in this, with greater certainty of exclusion of sulphur from coal gas. A blank experiment must always be carried out with the same quantities of reagents as used in the actual analysis, as magnesia usually (and bromine occasionally) contains a little sulphate. Fusion with sodium peroxide has also been recommended.[2] Neither the Eschka nor peroxide methods give satisfactory results with solid bitumens high in sulphur and volatile matter, but the figures for coals with sulphur not exceeding 2 per cent. are accurate.

[1] *Z. anal. Chem.*, 1878, 17, 497; *J. Soc. Chem. Ind.*, 1889, 8, 361.

[2] S. W. Parr, W. F. Wheeler, and R. Berolzheimer: "A Comparison of Methods for the Determination of Sulphur in Coal," *J. Ind. Eng. Chem.*, 1909, 1, 689.

Arsenic is frequently present in coal and coke: methods for its estimation have been described by Thorpe,[1] and by M'Gowan and Floris.[2]

Phosphorus.—The estimation of phosphorus is necessary for metallurgical purposes only. From 1 to 2 g. of the ash is digested with nitric and hydrofluoric acids, the fluoride removed by evaporation to fumes with a slight excess of sulphuric acid, and this solution, after addition of nitric acid, is precipitated with ammonium nitro-molybdate in the usual manner.

Nitrogen.—Nitrogen is usually determined by the Kjeldahl method. From 0·8 to 1·0 g. of the very finely powdered coal is weighed into a 500 c.c. Kjeldahl flask, 1 g. of powdered yellow mercuric oxide (or 0·7 g. metallic mercury) added, together with 7 g. of potassium sulphate and 30 c.c. of concentrated sulphuric acid; the whole is kept boiling till the solution becomes clear and the heating then continued for another two hours—not less than four hours in all. After cooling, the contents of the flask are transferred to a second flask of about 1000 to 1500 c.c. capacity, and the first flask well washed out with water into the second. An excess of pure caustic soda solution (sp. gr. 1·25) is added, and 35 c.c. of a solution of yellow sodium sulphide, containing about 40 g. to the litre, together with some small capillary glass tubes closed at one end to prevent bumping. The whole is then slowly distilled for about one hour into a receiver containing 20 to 30 c.c. of decinormal sulphuric acid. The usual bulb arrangement for preventing spraying of the alkaline liquid is interposed between the distilling flask and the condenser. Towards the end of the distillation the condenser water is cut off and the distillation continued until the steam just reaches the standard acid. The excess of acid is titrated back with standard alkali, with methyl red as indicator. A. C. Feildner and C. A. Taylor[3] have compared the various modifications of the Kjeldahl method with the Dumas method. The latter tends to give high results partly on account of nitrogen derived from the copper oxide and partly owing to the fact that methane is with difficulty completely oxidised by hot copper oxide. Some of the modifications of the Kjeldahl method give low figures with coal, but with both mercury and potassium sulphate present as described above, the mean difference from the Dumas method was found to be 0·05 per cent.

Carbon and Hydrogen.—Owing to the hygroscopic properties of finely divided coal after drying, the combustion is best carried out on the air-dried fuel, with subsequent correction of the water found for the moisture present as such. Any error due to possible oxidation

[1] Thorpe, *J. Chem. Soc.*, 1903, **83**, 969.

[2] M'Gowan and Floris, *J. Soc. Chem. Ind.*, 1905, **24**, 265.

[3] "The Determination of Nitrogen in Coal," Technical Paper 64, U.S.A. Bureau of Mines, 1915.

during drying is thus avoided. The carbon and hydrogen are determined as in the ordinary ultimate analysis of organic compounds. Either a gas furnace or electric resistance furnace may be used. The

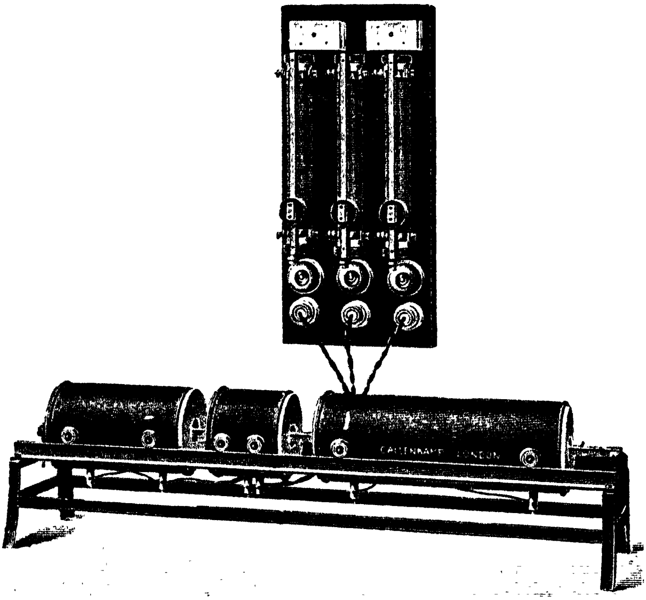

Fig. 177.

latter (Fig. 177) heats the combustion tube very evenly and regularly, and permits a definite temperature being attained more readily than with gas; glass tubes last longer in consequence. With a gas furnace, on the other hand, it is more easy to vary the temperature of sections of the combustion tube. The Fletcher furnace (Fig. 178) is very convenient as it can be built up in sections to any desired length and admits of control, not only in the usual way by the separate taps, but also by pushing in or out a section of the burners. A combustion tube of hard glass or fused quartz is used: *a*, *a* (Fig. 179) are two asbestos plugs,

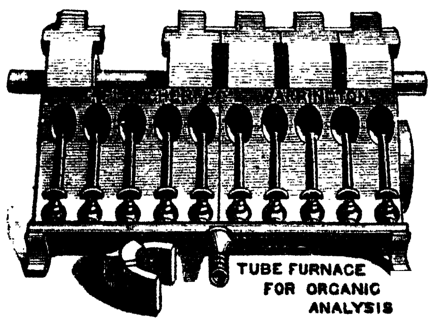

Fig. 178.

wrapped in very thin platinum foil, and between these is a layer, *n*, of copper oxide (granular or wire form), to which in the case of coal containing much sulphur is added a shorter layer of coarse lead chromate. This retains the sulphur, and, at a temperature just short of

fusion, burns traces of methane completely; copper oxide alone cannot be relied upon to oxidise methane completely (*cf.* (4), p. 261). If the coal is mixed with about ten times its weight of dry powdered lead chromate before being placed in the boat, most of the sulphur is retained and the combustion of the coke is more readily effected. It should be noted that fused lead chromate rapidly destroys both glass and quartz

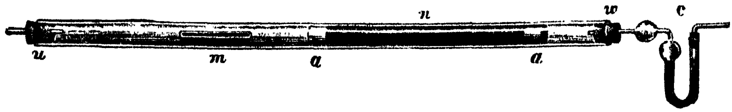

FIG. 179.

tubes. Before beginning the combustion proper, the tube is heated to low redness throughout its length, and a current of dry air freed from carbon dioxide passed through it for about fifteen minutes. The front part of the tube is allowed to cool, the boat containing the sample mixed with lead chromate introduced, the weighed absorption tubes attached, and the combustion then carried out in the usual manner in a current of oxygen. At the end of the combustion purified air is drawn through the tube to replace the oxygen in the weighed tubes.

THE DETERMINATION OF THE CALORIFIC POWER OF FUEL

The true calorific power of fuels can only be determined reliably by means of direct calorimetric measurements. There are three types of calorimeters in common use:—

(1) The fuel is mixed with a solid oxidising agent.
(2) The fuel is burned in a stream of oxygen at ordinary pressure.
(3) The bomb calorimeter, in which the fuel is burnt in oxygen under high pressure (20 to 40 atmospheres).

Lewis Thompson's Calorimeter, in which the fuel is oxidised by a mixture of potassium chlorate and nitre, has been very largely used in technical work. Comparison of the Lewis Thompson with other forms of calorimeter has been made by Brame and Cowan,[1] and by Gray and Robertson.[2] The former found that even after determining the unburnt coal left after combustion the errors were very large—2·3 to 6·4 per cent. The amounts of unburnt coal found with fuels of different types varied from 5·7 to 31·8 per cent., so that the errors of the instrument when used in the ordinary way without collecting and allowing for the unburnt coal are much larger. Gray and Robertson found deficits of

[1] J. S. S. Brame and W. A. Cowan, *J. Soc. Chem. Ind.*, 1903, **22**, 1230.
[2] T. Gray and J. G. Robertson, *J. Soc. Chem. Ind.*, 1904, **23**, 704.

from 1 to 13 per cent., and concluded that no constant correction is possible, and "at the best, the method may be taken to give a very rough indication of the heating value of bituminous coals." This instrument may therefore be regarded as obsolete, and has been largely replaced by an instrument of similar type in which sodium peroxide is used as the oxidising agent.

Parr's Calorimeter.—In this apparatus the sample is burnt with sodium peroxide. A nickel-plated vessel A (Fig. 180), of about 2 litres capacity, serves as the calorimeter. This is placed inside a wooden vessel C, which itself stands in a similar vessel B. The two air-spaces, *a* and *b*, and the double cover G, containing an air-space *g* and the wood material of the vessels, provide sufficiently for all practical purposes, against loss of heat. The reaction vessel D (Fig. 181) consists of a strong nickel-plated brass cylinder, the ends of which are provided with leather washers and can be firmly screwed on; it has a capacity of about 35 c.c. The base J rests on a conical support F, forming part of the inner vessel E; from the upper end of D passes the tube H, which extends right through the cover G, and is provided with a pulley P. A series of four small propeller blades, *hh*, is attached by spring clamps to D, which is rotated by means of a water turbine, and by employing a sufficiently high speed the water can be kept in circulation through E in the direction of the arrows; a thorough mixing is thus produced, and an even temperature maintained. The blades *h* are so fixed as to cause the current to flow downwards next to the cylinder D and upwards outside E, when the rotation is right-handed. Inside the tube H (Fig. 181) is a narrower tube L, notched on one side and continued downwards to a conical valve K. By the action of a spiral spring M, connection with the interior of D is cut off, unless the tube L is depressed by pressure at N; any escape of gases during combustion is thus prevented. Ignition of the charge is brought about by dropping a red-hot piece of iron wire into L, then sharply depressing N, when the wire drops through K into D. A delicate thermometer, held in position by a thick rubber ring and reaching about half-way down the vessel A, is passed through a hole 8 to 9 mm. wide in the

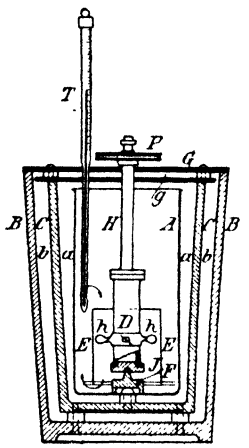

FIG. 180.

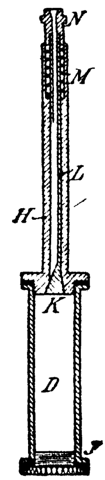

FIG. 181.

cover G. The double vessel B C is placed on a firm table, within reach of the necessary motive power. Two litres of water are poured into A before it is placed into position, so as to avoid water being splashed into C; for if the outer side of A or the inner portion of C should be moist, this would ultimately produce an error in the results, owing to evaporation. The temperature of the water should be about 2° below the temperature of the room. A is carefully set into C, and is then ready to receive the reaction vessel D.

The latter is carefully dried internally and externally, which is best done by gently warming on a sand-bath or hot-plate; the base J is screwed on and tightened with a key. About 10 g. of sodium peroxide (passed through a sieve of 1 mm. mesh) is then introduced. This reagent is best kept in a wide-mouthed stoppered bottle, along with a small measuring vessel, supplied with the instrument; the measuring vessel, which holds 10 g. of the reagent, is made of nickel-plated brass, and is provided with a small handle.

After introducing the sodium peroxide into D, 0·5 to 1 g. of the coal sample, together with any other necessary reagents, is put in, the cover screwed on, and the whole well shaken, K being kept closed by an upward pressure of the finger on N, otherwise a small quantity of the mixture may be shaken into L. The vessel is then tapped, to bring the whole of the mixture to the bottom, the working of K tested to see that it acts smoothly, and the blades *h* clamped on; D is then placed inside A so that it rests on the conical peg at the bottom.

Lunge[1] recommends the following method for carrying out the determination:—

The coal to be tested is powdered, and should be passed through a wire sieve of 0·3 mm. mesh; a more finely divided sample of hard coals and anthracite should be used, which may be obtained by placing a piece of bolting cloth under the wire sieve. Lignite must be previously dried, for about an hour, at a temperature of 105° to 110°; exactly 1 g. of this substance is then weighed out and shaken into the reaction vessel, previously charged with the 10 g. of sieved sodium peroxide, after which the vessel is closed and shaken for one to two minutes, as described above. Bituminous coals do not require previous drying, unless the moisture exceeds 2 to 2½ per cent. In the case of coal, exactly 0·5 g. is weighed out, and to this is added exactly 0·5 g. of finely powdered pure tartaric acid; this mixture is then added to the usual 10 g. of the peroxide. The addition of potassium persulphate, which has been suggested as necessary for the combustion of hard coals and anthracite, is regarded by Lunge and Grossmann[2] as superfluous and as the source of discordant results.

[1] *Z angew. Chem.*, 1901, 14, 794 and 1270; 1903, 16, 911; 1905, 18, 1249.
[2] *Ibid.*, 1905, 18, 1249.

The cover G having been placed in position, the pulley P is attached, and the thermometer inserted in the cover, as shown in the figure. The turbine is then set in motion so that the pulley revolves clockwise. A speed of about 150 revolutions per minute is kept up until the thermometer shows a constant temperature, which takes about three minutes; this temperature is noted, and the motor is kept running at the same speed till the conclusion of the experiment.

Ignition is effected by means of a piece of red-hot iron wire, 2·5 mm. in diameter and 10 mm. long; a piece of this size should weigh about 0·4 g., and the same piece can be used a good many times before its weight falls much below 0·4 g. Experience has shown that soft iron is more suitable for the purpose than nickel, copper, silver, or platinum. It does not melt, as the first three of these do, forming peroxides, but it becomes covered, when first used, with a hard, black, adhesive coating of the magnetic oxide, which protects it for a considerable time. Using the above weight, and at a temperature of say 700°, the heat introduced by the iron amounts to $0{\cdot}4 \times 0{\cdot}12 \times 700 = 33{\cdot}6$ calories, corresponding to a temperature rise in the calorimeter of 0°·016. As the readings are carried out to 0°·005, a constant deduction, fixed at 0°·015, is made. The wire, held pointing downwards with a pair of bent tweezers, is heated to redness and dropped through N; N is then sharply depressed with the tweezers, so that the iron passes through K, without permitting any escape of gas through L. A hissing noise, lasting for several seconds, denotes the combustion of the charge, and the thermometer rises, at first rapidly, then more slowly; after about four or five minutes the maximum temperature is attained, which remains constant for about five minutes, when the reading is taken. The experiment is then finished. The motor is stopped, the thermometer, pulley, and cover are taken off, the vessel A, with contents, is taken out bodily, and the agitators *hh* are removed from D, which is taken to pieces and placed in a basin of warm water to dissolve out the contents. On neutralising the solution so obtained, with hydrochloric acid, the presence of any unburnt fuel can be detected; should any be present, the results are worthless.

Calculation of results. The water value of the instrument was 123·5 g.; including the water, therefore, the total value is 2123·5 g. Of the rise in temperature $t'-t$ produced, t' being the final and t the initial temperature of the calorimeter, 72·5 per cent. is regarded as due to the combustion proper, and 27·5 per cent. to the reaction of the products of combustion with the sodium peroxide and oxide. When 1 g. of the fuel is burnt, as in the case with lignite, the number of calories produced is thus $0{\cdot}725 \times 2123{\cdot}5\ (t'-t) = 1540\ (t'-t)$. It is simply necessary therefore to subtract 0°·015 from the recorded value, $t'-t$, on account of the heat introduced by the iron wire, and to multiply by 1540; the

result gives the calorific power in centigrade units. With coal, only 0·5 g. is used, so that the recorded temperature difference is multiplied by $1540 \times 2 = 3080$. It is necessary first, however, to subtract the heating due to the combustion of 0·5 g. of tartaric acid, and that due to the iron; careful experiments have shown this to be 0°·832. If the sodium peroxide contains an excessive amount of moisture, as may be the case if a considerable quantity of peroxide is kept and frequently opened for use, the results will come out too high. It is then necessary to make a blank test, using 0·5 g. of tartaric acid, and about two-thirds of a measure (about 7 g.) of sodium peroxide. If the calorimeter temperature rises more than 0°·832, it will be necessary, in future use of this stock, to take such extra rise into consideration, by allowing 0°·15 for every 0°·1 excess rise obtained in the blank experiment (0°·15 being, of course, the allowance for a full measure of 10 g. of peroxide).

Parr's method of determining calorific power is more convenient, cheaper, and far simpler in manipulation, than any of the processes involving the use of a bomb, but it has certain obvious defects. In the first place, the combustion may be either too violent or incomplete, if the proportion of added materials is not appropriately adjusted; secondly, the heat generated by the absorption of the water and carbon dioxide, formed in the combustion by the sodium peroxide, has to be determined empirically for each instrument; and thirdly, the value of the coefficients given above does not hold for all kinds of coal, and still less for other fuels, such as lignite, petroleum, etc. These points have been specially investigated by Lunge and Offerhaus,[1] and by Lunge and Grossmann.[2] The latter conclude that the method is unreliable for coals having a calorific value less than 7500 cals. For coals having a higher calorific value, the method is of practical value, under the conditions given above. Both the coal and the sodium peroxide must be finely powdered and intimately mixed, and the peroxide must be of good quality. The heat value of the tartaric acid, together with that of the ignition wire, to be subtracted from $t'-t$ should be 0°·832, as given above, instead of 0°·85 previously accepted, and the coefficient should be 1540 as stated, in place of 1550 as formerly used. The latter value holds, of course, only for a calorimeter of the water value 2123·5 when charged.

Langbein discards Parr's process as altogether unreliable, but Lunge holds that this conclusion is not justified. The instrument has been much used by engineers, but as 27·5 per cent. of the heat produced is due to secondary reactions, which percentage depends on the quality and treatment of the sodium peroxide, and there is another large corrective term depending on the purity of the tartaric acid, the sodium peroxide calorimeter is not much used by chemists.

[1] *Z. angew. Chem.*, 1903, **16**, 911. [2] *Ibid.*, 1905, **18**, 1249.

Combustion in Oxygen at Ordinary Pressure.—The earliest determinations of calorific value were made with instruments of this type. Lavoisier and Laplace, in 1780, determined the heat of combustion in this way. Many forms of this instrument have been described. Favre and Silbermann recognised that combustion was not complete, and modified the calorimeter to allow for this. Schwackhöfer devised a still more complicated form (1884), but since that date there has been a tendency to revert to simpler forms. If it is remembered that owing to the necessity of using a glass containing vessel no accurate correction

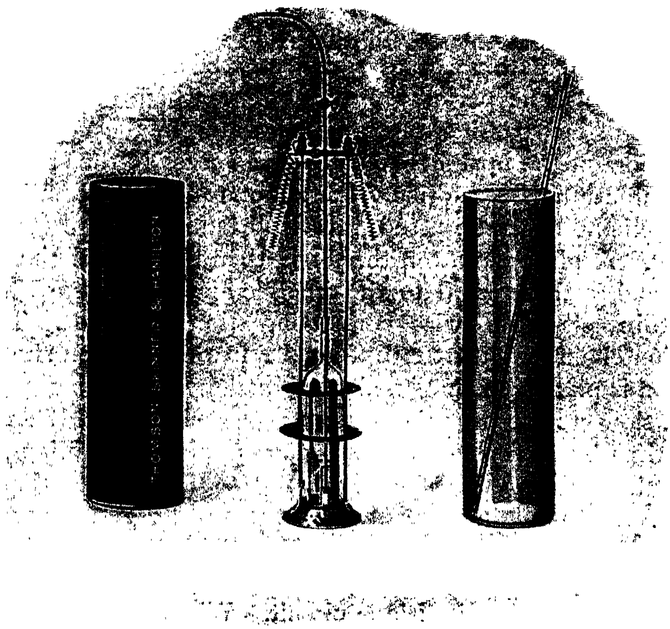

FIG. 182.

for cooling can be made, and also that a small but indefinite amount of fuel escapes complete combustion, then the simplest type consistent with efficient cooling of the combustion gases is the best, especially if the same instrument is used empirically after calibration with a coal of the same class and of calorific value known from combustion in a bomb calorimeter.

Gray's Calorimeter. The instrument[1] described by T. Gray[2] is simple in construction, and has been shown by Gray and Robertson[3] to give results within 1 per cent. if standardised with coal of known heating value. (See Fig. 182.)

The coal is burnt in a small platinum crucible supported on a

[1] Made by Messrs Thompson, Skinner & Hamilton, Sauchiehall Street, Glasgow.
[2] *J. Soc. Chem. Ind.*, 1906, 25, 409. [3] *Ibid.*, 1904, 23, 1704.

metal ring in metallic contact with the metal base. The glass tube, 6½ inches long and 2 inches diameter, sits loosely clamped on the perforated metal base; the brass tube for supplying the oxygen passes through a thick-walled rubber tube fitted to the drawn-out end of the combustion chamber and may be fitted in position by tightening the thumbscrew. Two upright brass tubes, joined above by a vulcanite crosspiece and provided with terminals, transmit the current for the ignition of the coal. These tubes are in metallic connection with the metal base, and through one of them an insulated wire passes from the terminal to a short metal rod inside the combustion chamber. The upper end of this rod and of the one supporting the crucible are on a level slightly higher than the top of the latter, and are connected by means of a thin platinum wire which can be made red hot by the electric current. The perforated metal discs, which serve to break up the bubbles of gas passing through the water in the calorimeter, are made to slide on the uprights so as to give access to the crucible. For the determination of a calorific value about 1 g. of the coal is weighed out approximately, compressed into a briquette, and then weighed accurately. A piece of cotton thread is then tied round the briquette and the coal is transferred to the crucible and the cotton thread tied to the thin platinum wire connecting the two rods. The glass combustion chamber with the brass tube in the position shown in the illustration is placed on the stand and fixed by tightening the thumbscrew; a slow current of moist oxygen is passed through the apparatus, which is then immersed in the calorimeter beaker containing two litres of water, the temperature of which is $1^\circ{\cdot}5$ to $1^\circ{\cdot}75$ lower than that of the room. After an interval of ten minutes the temperature of the water is read to $0^\circ{\cdot}01$, the oxygen current is increased so that a rapid stream of gas passes and the cotton fuse is ignited by pressing the key which closes the ignition circuit. When the combustion is complete the rubber tube connecting the oxygen supply to the calorimeter is detached so as to allow the water to enter the combustion chamber, and connection is again made with the oxygen supply to continue the mixing, and the maximum temperature is observed. The appearance of unburnt tarry matter is an indication that the current of oxygen was not sufficiently rapid. The oxygen is passed through a wash-bottle containing water, to saturate the gas, and the correct rate is obtained by inserting a T-piece between the wash-bottle and the calorimeter, the upright limb of the T dipping in a column of water. The rate of flow of oxygen depends on the jet and the length of this column. The correct height of column is supplied by the maker. The water value should in every case be determined from the mean of a number of combustions of an average coal of known calorific value. In a comparison of an instrument

of this type with the bomb calorimeter, Gray and Robertson[1] show that consecutive determinations with the same coal vary by 100 to 150 calories, or from 1·5 to 2 per cent. If the instrument is standardised with coal, the values are from 0·04 per cent. to 1·1 per cent. low. This represents the accuracy attainable in skilled hands; in inexperienced hands, if the oxygen is supplied too slowly with bituminous coals there may be tarry matter deposited, and with anthracitic coals it is difficult to avoid unburnt carbon in the residue.

The Bomb Calorimeter.—The first calorimetric bomb was due to Andrews, who used it for the determination of the heat of combustion of hydrogen and oxygen. Later Berthelot adopted the same method for other combustible gases, and then modified his instrument so that liquid and solid substances could be burnt. This instrument was used in a long series of thermochemical researches. The Berthelot bomb was made of steel, lined internally with thick platinum foil, and heavily nickel-plated externally. Mahler replaced the platinum lining with enamel, and this lining is usual in the types of bomb now in use. Parr dispenses with enamel, and uses a special acid-resisting alloy in the construction of the bomb. The composition of the enamel used is not a matter of indifference; some enamels containing sodium sulphate as a constituent have been used, and these always give appreciable amounts of sulphates in the bomb washings. This renders such instruments useless for sulphur determinations, and also vitiates the corrections for the calorific value. It has been recently shown that the correction for nitric acid formed may also be disturbed by the extraction of basic substances from the enamel lining, although this appears to be most marked with a new bomb, and to become negligible after long use. Numerous types of calorimetric bomb are now obtainable: the one shown in Fig. 183, due to Kroeker,[2] has the advantage of also serving

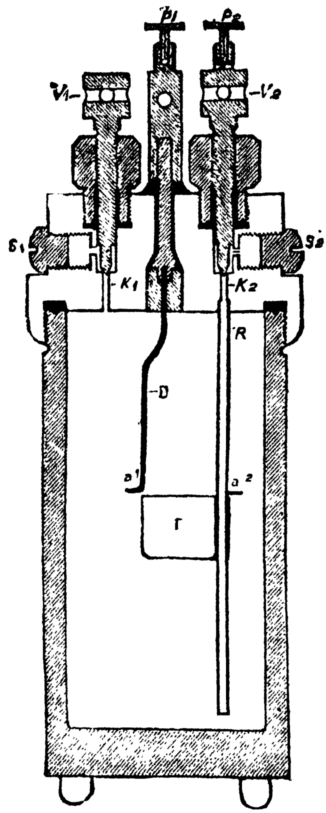

FIG. 183.

[1] *J. Soc. Chem. Ind.*, 1904, 23, 704.

[2] Bestimmung der nutzbaren Verbrennungswärme der Brennstoffe, *Z. Ver. deut. Ruben zuckerind.*, 1896, p. 177.

for the determination of carbon and hydrogen (the latter only approximately) and is widely used. The body is of steel, of about 300 c.c. capacity, and externally nickel-plated. The lid, made of bronze, carries two valves, from one of which a platinum tube, R, extends nearly to the bottom of the body. A third hole through the cover carries an insulated rod, the continuation of which, D, is of platinum. The platinum tube carries the capsule, T, of platinum or quartz, and a projection for conveniently holding the fuse wire. Connection to the compressed oxygen cylinder is made at S_1 or S_2, preferably the latter, as there is less chance of portions of the combustible being blown out of the capsule by the stream of incoming gas. It is not advisable to burn a solid combustible in powdered form, as portions are apt to be thrown out of the cup during burning. This may lead to incomplete combustion, with a corresponding deficit in the calorific value found; and, a more serious matter, some of the material may be thrown out of the capsule and burn on the sides of the bomb and damage the enamel. Hence it is usual to compress the material into a briquette in a small screw press. This briquette, after weighing, is placed in the capsule, T, the connections made to ensure firing, 10 c.c. of water placed in the bomb, and the head screwed on. A cylinder of compressed oxygen is connected to S_2 and the gas slowly admitted until the manometer shows 25 or 30 atmospheres pressure. After disconnecting the oxygen cylinder, the screw, S_2, is replaced, and the bomb is then placed in the calorimeter vessel containing a weighed quantity of water (sufficient to make the water equivalent of the whole about 2500), absence of gas leakage proved, the electrical connections made, and the stirrer fitted. The calorimeter vessel stands in a double-walled copper jacket holding about 25 litres of water, the temperature of which is assumed to remain constant throughout the experiment. The calorimeter thermometer is usually divided to $0^\circ{\cdot}01$ and readings made to $0^\circ{\cdot}001$ C. The stirrer is worked by a motor at a uniform rate (about 120 oscillations per minute), and as soon as the thermometer is steady, readings are commenced and taken at one-minute intervals. The fuse is fired at the fifth minute and readings continued for fifteen minutes in all. The readings may be conveniently entered on a form similar to that on p. 349.

The calculation of the terms θ, v, nv, $\Sigma_1^4(\theta)$, $\frac{1}{2}(\theta_0+\theta_5)$, and θn can be made during the intervals between the readings, and the remaining terms can be worked out in two or three minutes. The cooling correction is based on the Regnault-Pfaundler formula:—

$$\text{Correction} = nv + \frac{v'-v}{\theta'-\theta}[\Sigma_1^4(\theta) + \tfrac{1}{2}(\theta_0+\theta_5) - n\theta]$$

in which n is the number of time intervals in the chief period (five in the example given), v and v' the rates of cooling in the preliminary and

after periods respectively, θ and θ' the mean temperatures of the preliminary and after periods.

Date: 23rd November 1914.	Capsule + fuel = 7·8750 g.	Thermometer: No. 1.
Number: 585 B.	Capsule = 7·0200 g.	Temperature (final): 15·0.
Substance: Oil.		Water: 2160 g.
Ash: —.	Weight = 0·8550 g.	W.E.: 2500 g.

Preliminary Period.		Chief Period.		After Period.	
Time.	Temperature.	Time.	Temperature.	Time.	Temperature.
0	0·026	6 θ_1	2·00	10 θ_5	3·598
1	0·030	7 θ_2	3·47	11	3·594
2	0·033	8 θ_3	3·60	12	3·590
3	0·037	9 θ_4	3·599	13	3·586
4	0·041			14	3·583
5 θ_0	0·045	$\Sigma_1^4(\theta)$	= 12·67	15	3·578
		$\frac{1}{2}(\theta_0+\theta_5)$	= 1·82		
θ	0·035	$-n\theta$	= −0·17	θ' = 3·588	
v	−0·0038			v' = +0·0040	
nv	−0·019	S	= 14·32	$k=\dfrac{v'-v}{\theta'-\theta}=\dfrac{+0\cdot0078}{+3\cdot55}=+0\cdot0022$	

Cooling correction $= nv + kS = -0\cdot019 + 0\cdot0314 = +0\cdot0124$.

		Calibr.
Uncorrected rise $(\theta_5-\theta_0)$	3·598°	+0·0069°
	0·045°	−0·0000°
	3·553°	+0·0069°
Thread . .		−0·0079°
Cooling . .		+0·0124°
Nitric acid . .		−0·0048°
Sulphur . .		—
Total correction . =	+0·007°	
Corrected rise .	= 3·560°	

Rise per grm. $=\dfrac{3\cdot560°}{0\cdot855}$
R = 4·164°
R × 2500 = 10,410 cal. per grm.
R × 4500 = 18,740 B.T.U. per pound.

For ignition fine wires of iron, nickel, or platinum have been used. Iron is objectionable, as the molten globules of ferric oxide perforate the enamel or platinum lining. Fine platinum wire (·002 to ·0025 inch) is preferable; it may be embedded in the briquette (Hempel), or, more simply, a measured length of cotton thread may be tied round the wire and the end placed in contact with the fuel. The heat of combustion of the thread is allowed for as above.

For further details regarding calorimeter corrections, see G. N. Huntly, "The Accuracy obtainable in Fuel Calorimetry,"[1] and "Corrections in Bomb Calorimetry."[2] Adiabatic calorimeters, in which the correction for cooling is abolished, have been described by Richards, Henderson, and Forbes;[3] Richards, Henderson, and Frevert;[4] Benedikt and Higgins;[5] and J. A. Riche.[6]

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 917.
[2] *Analyst*, 1915, **40**, 41.
[3] *Z. physik. Chem.*, 1905, **52**, 551.
[4] *Z. physik. Chem.*, 1907, **59**, 532.
[5] *J. Amer. Chem. Soc.*, 1910, **32**, 461.
[6] *J. Amer. Chem. Soc.*, 1913, **35**, 2747.

The determination of the water equivalent of the bomb is best made by standardising with substances of known calorific value. Benzoic acid, cane-sugar, or naphthalene are usually employed for this purpose, and of these benzoic acid is preferable. In the United States the Bureau of Standards issue a benzoic acid with a stated calorific value, but, up to the present, no corresponding standard substance for standardising bomb calorimeters has been issued in Great Britain. A comparison of various samples of benzoic acid of German and English origin, however, has not shown differences greater than 0·2 per cent. from the American standard.[1]

The value furnished by the calorimeter is the so-called *gross calorific value.* This is a direct experimental figure: the *net value* or *lower value* is obtained by deducting from the gross value a figure depending on the percentage of hydrogen present in the fuel. If the products of combustion escape at a higher temperature than 100° C., the water escapes as steam, and the deduction corresponds to the latent heat of vaporisation of the water formed. Unfortunately, there is no general agreement in the definition of the "net value"; the Institution of Civil Engineers gives the following: "The net calorific value used for calculating the boiler efficiency will be the gross value, less the latent heat, reckoned at 1055 B.T.U. per lb. of the water condensed from the products of combustion by cooling to 60° F., and can be found from the following formula:—
Net calorific value per lb. of fuel = gross calorific value minus 1055 (lbs. of moisture per lb. of fuel + 9 × lbs. of hydrogen per lb. of fuel)"—the contents of the bracket representing the lbs. of water vapour produced per lb. of fuel. Until an international definition of the net value has been agreed upon, the use of the gross value only is preferable.

Corrections for Nitric Acid and Sulphur. During the combustion in the bomb any sulphur in the fuel is converted into sulphuric acid; some nitric acid is also found in the washings from the bomb produced from nitrogen present in the oxygen and from nitrogen in the fuel. It is conventionally assumed that no nitric acid is produced when the fuel is burnt under a boiler, and that the sulphur, when burnt in air at the ordinary pressure, escapes as sulphur dioxide. Hence an approximate estimation of the amounts of nitric and sulphuric acids in the bomb washings is made, and the corresponding small deductions are made from the observed calorific value. The nitric acid neutralised by 1 c.c. of decinormal alkali represents 1·43 calories, and for each 1 per cent. of sulphur in the fuel a deduction of 22·5 calories represents the extra amount of heat found in the bomb combustion due to the conversion of gaseous sulphur dioxide into dilute sulphuric acid. An alternative mode of applying these corrections is given in the

[1] The international value for heat of combustion of benzoic acid is 6329 ± 2 calories per gram (at 20°) in air = 6324 calories at 15° since 1 calorie at 15° = ·9992 calorie at 20°. See Dickenson, Bull. Bureau of Standards, 1914, **11**, 243.

example; for a water equivalent of 2500 the amounts of sulphuric and nitric acids, expressed as cubic centimetres of decinormal alkali, can be reduced to degrees and taken off as shown.

The quantity of nitric acid and of sulphuric acid produced may be determined volumetrically. The bomb washings, which are heavily charged with carbon dioxide, must be freed from this by prolonged boiling, and the hot liquid titrated with decinormal baryta, using phenolphthalein as indicator. The volume of baryta taken represents the sum of the two acids. An excess of decinormal sodium carbonate is now added, the solution gently boiled down and allowed to stand, filtered, and the excess of alkali in the filtrate titrated with decinormal hydrochloric acid. As an example, the bomb washings from the combustion of 1·001 g. of coal, after freeing from carbon dioxide, took a volume equivalent to 15·2 c.c. of decinormal baryta; 20 c.c. of decinormal sodium carbonate was then added, the liquid boiled down to about half its volume, filtered and washed. The filtrate took 11·2 c.c. of decinormal hydrochloric acid to neutralise to methyl orange. Hence the nitric acid took $20{\cdot}0 - 11{\cdot}2 = 8{\cdot}8$ c.c. The sum for the two acids was 15·2 c.c. Hence the sulphuric acid took 6·4 c.c., and the sulphur is $6{\cdot}4 \times {\cdot}0016 = 0{\cdot}0102$ g. or 1·02 per cent. = 23 calories; nitric acid correction $8{\cdot}8 \times 1{\cdot}43 = 12{\cdot}6$ calories; total to be subtracted, 36 calories. A better method, if an accurate figure for the sulphur is required, is to add a measured volume of decinormal sodium carbonate in excess, boil gently down to a small volume, filter, wash, and titrate the excess of alkali with decinormal acid. The sulphur is then precipitated in the usual way with barium chloride.

Heavy oils and non-volatile liquids may be safely burnt in the open cup, but special methods must be adopted for volatile liquids. One method, used by Berthelot,[1] is as follows. A small test-tube is dipped into liquid collodion, which is allowed to dry partially one or more times until a coherent bag of collodion is formed outside the tube; this is dipped into water and the bag removed and allowed to dry. The bottom is then cut off and the collodion cylinder fixed to the upper portion of the platinum cup, using a little liquid collodion as cement. After gently drying, the mouth of the bag is drawn together with a thin platinum wire and the whole then weighed. The liquid is introduced with a fine pipette without wetting the collodion cap, the bag closed with the wire, and the whole weighed, placed in the bomb and the combustion carried out in the usual manner. Alternatively, the liquid may be sealed in a glass tube. The technique is delicate, and for full details reference may be made to papers by T. W. Richards and H. S. Davis,[2] W. A. Roth and H. Wallasch,[3] and T. W. Richards and R. H. Jesse.[4]

[1] *Traité pratique de Calorimetrie Chimique*, 2nd edition, p. 270.

[2] *J. Amer. Chem. Soc.*, 1917, **39**, 341-354.

[3] *Annalen*, 1915, **407**, 134.

[4] *J. Amer. Chem. Soc.*, 1910, **32**, 268.

The Calorific Value of Gaseous Fuels

The calorific value of power gas or illuminating gas can be calculated from the calorific values and proportions of its constituents, but the method involves a complete gas analysis, and is unsatisfactory for coal gas, since the calorific value of the "heavy hydrocarbons," the highest per unit volume, is not exactly known.

For power gas (producer gas, generator gas, water gas, etc.), this objection applies with less force, and frequently where a small gas sample has to be carried a considerable distance this is the only method available. In Great Britain, under the Gas Regulation Act, 1920, a standard illuminating power has been abolished, and gas is now to be sold by the therm (100,000 British Thermal Units), and it is probable that the sale of gas by therms instead of by volume will become general in all countries.

A great deal of ingenuity has been spent on the design of gas calorimeters. J. H. Coste, in his work on *The Calorific Power of Gas*, gives a description of about twenty, and this number might easily be doubled at the present time. The Junkers calorimeter, described in detail in the last (1908) edition of this book, is largely used on the Continent and in America. It will be sufficient to describe the instrument generally in use in Great Britain.

Boys's Gas Calorimeter.[1]—This apparatus[2] is prescribed by the *Metropolitan Gas Referees* (1918), for testing the calorific value of illuminating gas. It has been designed with the object of providing ample space for the circulation of the stream of gases, so that they pass slowly and freely through the instrument, and are thus effectively exposed to the cooling surfaces. The water content of the instrument is reduced to the smallest quantity, so that the outflowing water attains its steady temperature very quickly after the gas is lighted. The whole of the circulating water takes the same course continuously, being debarred from any parallel or alternative routes, and thus unequal heating and the attendant irregularity of the temperature at the outflow are avoided. The small content of water suffices to abstract the whole of the heat from the slowly travelling stream of gases, owing partly to the avoidance of parallel routes, but mainly by reason of its flow through a pipe of small diameter, the heat-collecting power of which is greatly increased by attached wires. The calorimeter is shown in vertical section in Fig. 184. It consists of three parts, which may be separated, or which, if in position, may

[1] *Roy. Soc. Proc.*, 1906, 77, [A], 122; and Notification of the Gas Referees, H.M. Stationery Office, 1918. The description which follows is largely taken from the latter publication, by permission of the Controller of H.M. Stationery Office.

[2] Made by Messrs J. & J. Griffin, Kemble Street, Kingsway, London, W.C.

be turned relatively to one another about their common axis. The parts are (1) the base, A, carrying a pair of burners, B, and a regulating tap. The burners are made of steatite, and they are carried upon a head and tube V, also made of steatite, and circular in cross section. The upper surface of the base is covered with a bright metal plate, held in place by three centering and lifting blocks, C. The centre of this plate is perforated and carries a ferrule, W, over which is slipped a tube of fibre, X, as shown. A recess 6 inches in diameter and $\frac{3}{4}$ inch deep is turned out of the base, and a disc of felt, Y, $5\frac{1}{2}$ inches in diameter and $\frac{3}{8}$ inch thick, and perforated in the centre, is fastened centrally in the recess. Six $\frac{1}{2}$-inch holes, Z, are drilled from the corner of the recess to the groove in the base. The blocks, C, are so placed as to carry (2) the vessel D, which must rest upon the horizontal portion of the blocks and be centred by their upturned ends. This vessel is provided with a central copper chimney, E, and a condensed water outlet, F. It is jacketed with felt, R, protected by a sheet of metal, S.

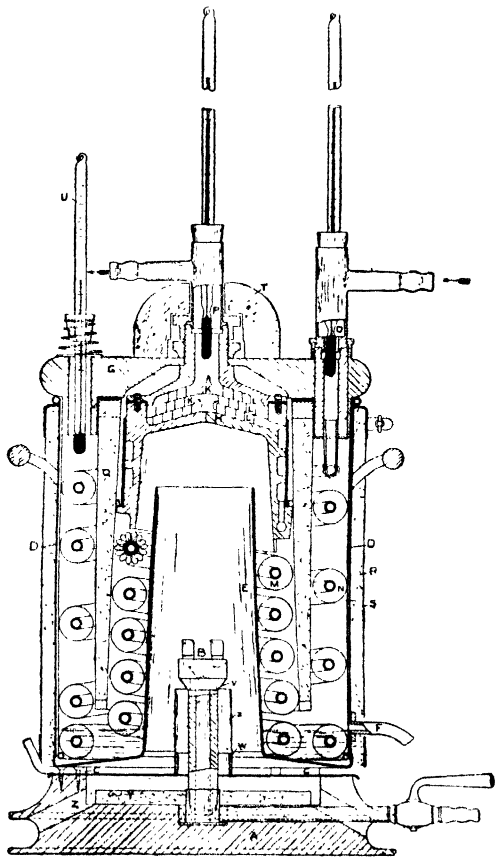

FIG. 184.

In order to prevent obstruction of the flow of condensed water from the outlet, F, a small dimple is punched in the outer casing on either side of the outlet, F, so as to project inwardly about $\frac{1}{16}$ inch. Resting upon the rim of the vessel, D, are (3) the essential parts of the calorimeter, attached to the lid G. At the centre, where the outflow is situated, there is a brass box, which acts as a temperature-equalising chamber for the outlet water. Two dished plates of thin brass, K, are held in place by three scrolls of thin brass, L, L, L. The lower or pendent portion of the box is kept cool by water, circulating through a tube which is sweated on to the outside of the bell. Connected to the water channel at the lowest

point, by a union, are six turns of copper pipe, such as is used in a motor-car radiator, of the kind known as Clarkson's. In this, a helix of copper wire threaded with copper wire is wound round the tube, and the whole is sweated together by immersion in a bath of melted solder. A second coil of pipe of similar construction, surrounding the first, is fastened to it at the lower end by a union. This terminates at the upper end in a block, to which the inlet water box and thermometer holder are secured by a union, as shown at O. An outlet water box, P, and thermometer holder are similarly secured above the equalising chamber, H. The lowest turns of the two coils M N are immersed in the water, which in the first instance is put into the vessel, D.

Between the outer and inner coils M N is placed a brattice, Q, made of thin sheet brass, containing cork-dust, to act as a heat insulator. The upper annular space in the brattice is closed by a wooden ring, and this end is immersed in melted rosin and beeswax cement, to protect it from any moisture which might condense upon it. The brattice is carried by an internal flange, which rests upon the lower edge of the casting, H. A cylindrical wall of thin sheet brass, a very little smaller than the vessel D, is secured to the lid, so that when the instrument is lifted out of the vessel and placed upon the table, the coils are protected from injury. The narrow air-space between this and the vessel D also serves to prevent interchange of heat between the calorimeter and the air of the room.

The two thermometers for reading the water temperatures, and a third, U, for reading the temperature of the effluent gases, are all near together and at the same level. The thermometer, U, for finding the temperature of the effluent gases is supported as shown in Fig. 184 by means of a cork and an open spiral of wire, so that the bulb is a short distance above the circulating coil, and with its stem passing through that one of the five holes provided for the effluent gases which is opposite the inlet water box as shown. The lid may be turned round into any position relatively to the gas inlet and condensed water drip that may be convenient for observation, and the inlet and outlet water boxes may themselves be turned so that their branch tubes point in any direction. A wood shield, T, made in two halves, serves to protect the outlet water box from loss of heat. The general arrangement of the apparatus, as set up for a test, is shown in Fig. 185, the gas being first passed through a meter and balance governor before being led to the calorimeter. The gas supply is connected up to the central tube at the back of the meter and thence to the governor, preferably by means of tin or composition piping. The pipe leading from the governor should terminate in a tap with a nozzle, to which a short length of rubber tubing is attached for connecting to the calorimeter.

A regular supply of water is maintained by connecting one of the

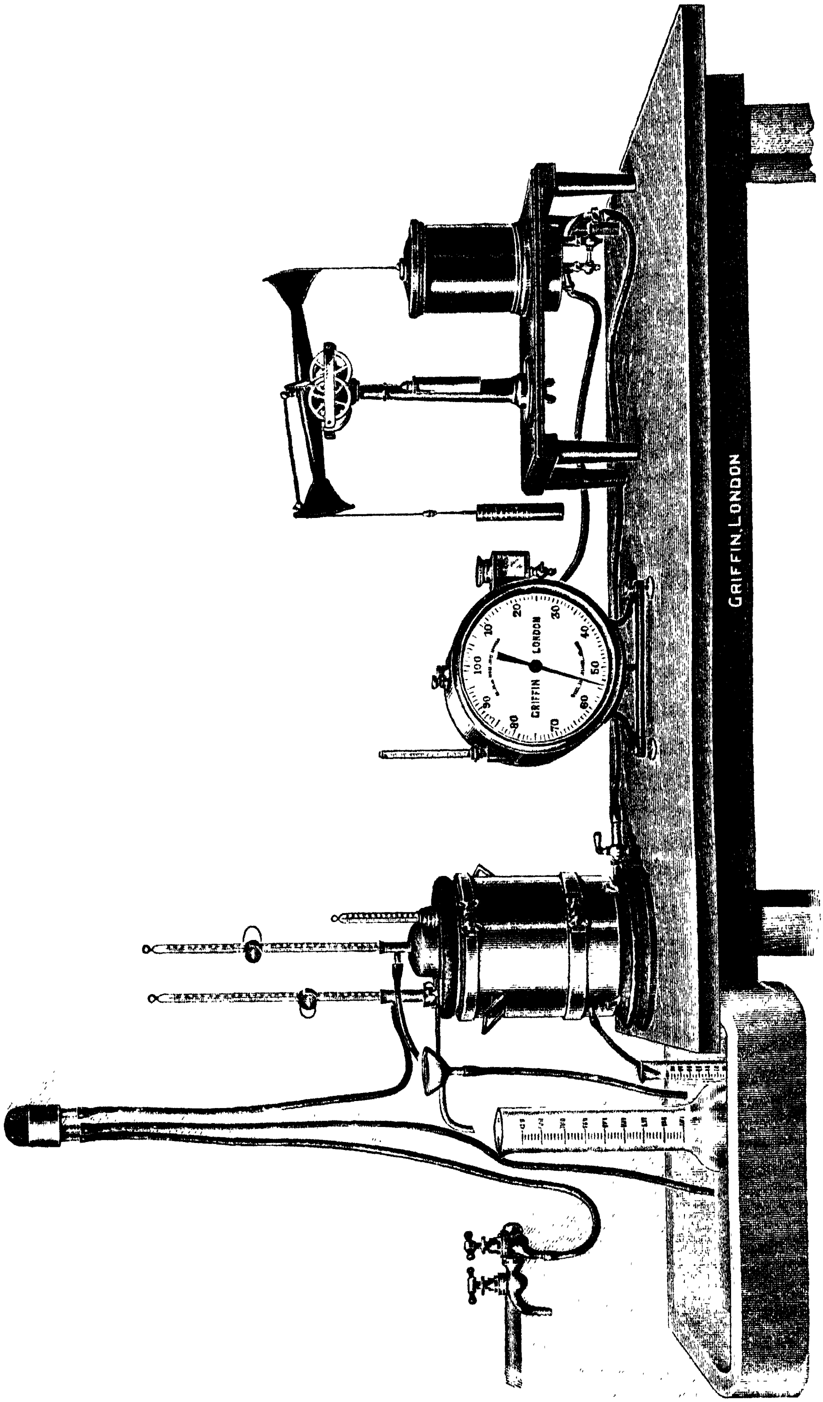

Fig. 185.

two outer pipes of the overflow funnel, shown in Fig. 185, to a small tap. The overflow funnel is fastened to the wall about 1 metre above the sink, and the other outer pipe is connected to a tube, in which there is a diaphragm with a hole 2·3 mm. in diameter. This tube is connected to the inlet pipe of the calorimeter. A piece of stiff rubber tubing, long enough to carry the overflow water clear of the calorimeter, is slipped on to the outflow branch, and the water is turned on so that a little escapes by the middle pipe of the overflow funnel, and is led by a third piece of tube into the sink. The amount of water that passes through the calorimeter in four minutes should be sufficient to fill the graduated vessel shown in Fig. 185 to some point above the lowest division (1600 c.c.), but insufficient to come above the highest division (2400 c.c.) in five minutes. If this is not found to be the case, a moderate lowering of the overflow funnel or reaming out of the hole in the diaphragm will effect the necessary correction. Before altering either adjustment, air bubbles should be removed from the rubber tube connecting the overflow funnel to the calorimeter by blowing at the water outlet tube. The overflow funnel should be provided with a lid to keep out dust.

The (centigrade) thermometers for reading the temperature of the inlet and outlet water are divided into tenths of a degree, and are provided with reading lenses, which slide on them. The thermometers are held in place by corks, fitting the inlet and outlet water boxes. The (Fahrenheit) thermometers of the wet and dry bulb hygrometer placed near the instrument, and the (Fahrenheit) thermometer for taking the temperature of the effluent gases, are divided only into degrees.

The flow of air to the burners is determined by the degree to which the passage is restricted at the inlet, at the outlet, and at the base of the brattice. The blocks C (Fig. 184) which determine the restriction at the inlet are made of metal $\frac{3}{16}$ inch thick, while the holes round the lid which determine the restriction at the outlet are five in number and are $\frac{5}{8}$ inch diameter.

The calorimeter should stand on a table by the side of a sink, so that the condensed water and hot water outlets overhang and deliver into the sink, as shown in Fig. 185. A glass vessel is provided of the size of the vessel, D, which should be filled with water, in which sufficient sodium carbonate is dissolved to make it definitely alkaline. The calorimeter, when not in use, is lifted out of its vessel, D, and placed in the alkaline solution, and left there until it is again required. The liquid should not come within 2 inches of the top of the vessel when the calorimeter is placed in it. The liquid must be replenished from time to time and its alkalinity maintained.

The measuring vessel, shown in Fig. 185, carries a change-over

funnel, which is placed beneath the short tube attached to the hot-water outlet. One side of the funnel delivers into the sink, and the other into a tube, which directs the water into the vessel.

Full details for carrying out a test are given in the Notification of the Gas Referees for 1918.

With the Boys's calorimeter, as with all continuous flow calorimeters, the gas is necessarily measured with a wet experimental meter, and the accuracy of the determination depends mainly on the care with which the meter is maintained in correct adjustment. The position of the thermometer in some types of wet gas meter is faulty, and this may give rise to an error of 0·5 per cent. on the volume measurement.

Recording Calorimeters.—A number of calorimeters which give a continuous record of the calorific value of a gaseous fuel are on the market. An extremely ingenious apparatus has been designed for this purpose by Prof. C. V. Boys.[1]

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[1] *Nature*, 1922, **110**, 251.

MANUFACTURE OF SULPHUROUS ACID, SULPHURIC ACID, AND NITRIC ACID

By J. T. DUNN, D.Sc., F.I.C., Consulting Chemist, Newcastle-on-Tyne, and the late Professor G. LUNGE

SULPHUROUS ACID

FORMERLY sulphurous acid was produced almost entirely for conversion into vitriol by the lead-chamber process; to-day it is made in considerable quantity in connection with the sulphite-cellulose industry, and to a lesser extent for conversion into liquid sulphur dioxide. On this account it is accorded separate treatment.

RAW MATERIALS

I. SULPHUR (NATIVE SULPHUR)

Sicilian native sulphur is shipped in the form of blocks, each weighing from 28 to 30 kilos; owing to the friable nature of the sulphur these blocks are usually shattered during transport into lumps of varying size and to some extent to powder. The best quality ("firsts," "prima Lercara" or "prima Licata") consists of large, shining pieces of amber-yellow colour. The second quality ("seconds," "seconda vantaggiata") is also of a good yellow colour, but not quite so brilliant in appearance. The bulk appears in commerce as a third quality ("thirds," "terza vantaggiata"); its colour is dull and not pure yellow. Nevertheless the ash is frequently as low as ½ per cent., and seldom exceeds 2 per cent.; in exceptional cases it may rise to 4 per cent. or more. The fourth grade is of a greyish-yellow colour, and may contain up to 25 per cent. of earthy matter. "Zolfo ventilato" is sulphur which has been ground, separated by an air blast, and sieved.

Commercial Sicilian sulphur contains only very small quantities of volatile matter and of bitumen, and generally is free from, or contains only traces of, arsenic and selenium. The sulphur from the Solfatara at Naples, which Phipson found to contain 11·162 per cent. of arsenic

and 0·164 per cent. of selenium, is of no importance as a commercial product. Louisiana sulphur sometimes contains petroleum.

The *degree of fineness* of ground sulphur must be determined when the sulphur is intended for application in vine culture to destroy the grape-disease *Oïdium.* This examination is effected by means of Chancel's *sulphurimeter*, shown in Fig. 186. The sulphurimeter consists of a cylindrical glass tube, 23 cm. long and 15 mm. diameter, sealed below, fitted with a glass stopper above, and graduated from the bottom upwards into 100 degrees. Each degree equals $\frac{1}{4}$ c.c.; the 100 degrees (25 c.c.) occupy a length of 100 mm. The ground sulphur is shaken with ether in the tube, and allowed to settle, when it forms a layer the height of which bears a relationship to the fineness of the grinding. The sulphur to be examined is first passed through a sieve of 1 mm. mesh, in order to break down the lumps formed during storage. Five g. of the sieved sulphur are placed in the tube, which is then half-filled with anhydrous ether as nearly as possible at a temperature of $17^\circ{\cdot}5$. The sieved sulphur in the tube is broken down still further by thorough shaking, after which ether is added until the level stands 4 mm. over the 100th division; the whole is again well shaken and the tube then fixed in a vertical position. When the sulphur layer has come to rest, its position on the scale is read off; the reading gives the fineness in "Chancel degrees." As a rule, ground sulphur shows 50° to 55°, finer qualities 70° to 75°, Zolfo ventilato 90° to 95°. For use in viniculture, a minimum of 60° and frequently of 75° Chancel is demanded.

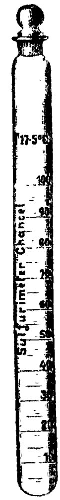

Fig. 186.

According to H. Fresenius and P. Beck,[1] the dimensions of the sulphurimeter are of importance and must be exact; they recommend the instrument made by J. Greiner, Munich. This differs in its dimensions from the French instrument described above; the length of the tube to division 100 is 175 mm., the length of the straight portion between 10° and 100° is 154 mm., and the internal diameter 12·68 mm. The ether employed should be distilled over sodium, and all disturbance should be avoided after the shaking, the instrument being immediately clamped in a stand and immersed in water at $17^\circ{\cdot}5$.

It may further be necessary to determine whether the fine sulphur intended for vine-dusting is really flowers of sulphur, or whether it consists of a mixture of ground sulphur with flowers of sulphur. This is best done by microscopic examination, the ground sulphur being distinguished by its crystalline appearance from the partially amorphous flowers of sulphur. The method is not, however, absolutely trustworthy,

[1] *Z. anal. Chem.*, 1903, 42, 21.

since flowers of sulphur change in course of time almost completely into the crystalline condition (Alpha sulphur). The partial insolubility of flowers of sulphur in carbon bisulphide may also be employed as a qualitative test, but with old samples the percentage of insoluble sulphur may occasionally be very slight. This reaction cannot be applied as a quantitative method, since the ratio between soluble and insoluble sulphur varies considerably even in freshly prepared flowers of sulphur.

Fonzes-Diacon[1] separates the sulphur into *gresil* (retained by a 100-mesh sieve), coarse flowers (passing 100-mesh but retained by 240-mesh), and fine flowers (passing 240-mesh), and determines the percentages insoluble in carbon disulphide in the *gresil* and in the coarse flowers. In pure sublimed samples the ratio of the first to the second of these is always less than unity (whether fresh or old, since any change on keeping affects all portions equally); but the addition of 20 to 25 per cent. of ordinary ground sulphur raises the ratio above unity.

Opinions differ very considerably as to whether ground sulphur or flowers of sulphur is the more efficient in viniculture. H. Fresenius and Beck recommend ground sulphur, maintaining that it adheres more firmly to the leaves than does the amorphous variety. In France, on the other hand, flowers of sulphur is preferred, owing to its finer state of division, as compared with the ground sulphur (which is frequently employed on account of its cheapness), and also because of the very active destructive action of the adhering acid on the *oïdium*.

The chemical examination of native sulphur includes the following determinations:—

1. **Ash.**—This is determined by burning off about 10 g. of sulphur in a tared porcelain crucible and weighing the residue.

2. **Moisture.**—In the case of lump sulphur this determination is frequently unnecessary, but it should be made if adulteration by spraying is suspected, or if the sulphur has been exposed to rain. The estimation is, however, always misleading, owing, on the one hand, to the difficulty of obtaining a genuine average sample, and on the other hand to the loss of moisture which almost inevitably occurs in breaking down the sample to suitable fineness for laboratory work. The sample should not be crushed further than to a coarse powder, and this should be done as speedily as possible. At least 100 g. should be taken for the estimation. In the case of ground sulphur, it is of course much easier to obtain an average and more finely divided sample. According to Fresenius and Beck, the drying operation should only occupy a short time and the temperature should not exceed 70°.

Difficulties in the moisture determination arising from the presence

[1] *Ann. Falsif.*, 1916, **9**, 333; *J. Soc. Chem. Ind.*, 1917, **36**, 333.

of gypsum have been experienced by F. B. Carpenter[1] in the examination of Mexican sulphur. He consequently recommends making the estimation by drying the sample *in vacuo* over sulphuric acid. A portion of the sample is freed from gypsum by boiling with dilute sulphuric acid, the residue dried and weighed, and the contained sulphur estimated, either by burning-off or by solution in carbon bisulphide (cf. *infra*).

3. **Bituminous substances.**—Any appreciable quantity is evidenced by the bad colour of the sulphur, but in most commercial sulphurs the amount present is too small to render a determination necessary. Sulphur recovered from gas residuals is, however, frequently quite black from the presence of this impurity.

H. Fresenius and Beck drive off the sulphur by heating 10 g. to slightly over 200°, weigh the residue, ignite for ash and re-weigh, and regard the difference between the two weighings as representing the organic matter present.

4. **Arsenic.**—This impurity may occasionally occur in very minute quantity in Sicilian sulphur, to a greater extent in the Solfatara sulphur (see p. 358), and especially in sulphur recovered from pyrites or from alkali-waste. The arsenic may be present either as arsenious sulphide, As_2S_3, or as arsenious oxide, As_2O_3; exceptionally also as calcium or iron arsenite. J. T. Conroy (private communication) finds the sulphur recovered from alkali-waste by the Chance-Claus process particularly free from arsenic; tested by the Hager method, only very minute and doubtful traces are indicated. Sulphur recovered from pyrites does not show such freedom.

For a qualitative examination for arsenic, Hager's method[2] may be employed. It is carried out by shaking 1 g. of sulphur with 15 drops of ammonium hydroxide and 2 c.c. of water, filtering after half an hour, and adding to the filtrate contained in a test-tube 30 drops of hydrochloric acid and 15 drops of a solution of oxalic acid. A strip of clean brass is then placed in the solution and this is warmed to a temperature of 60° to 100°; in the presence of arsenic an iron-coloured to black film forms immediately on the brass. A blank test should always be made with the reagents used, and to ensure uniformity of temperature it is advantageous to heat the two test-tubes side by side, in a beaker of water.

Sulphide and oxide of arsenic may be extracted by digesting the sulphur with dilute ammonia at 70° to 80°; they remain behind on evaporating the ammoniacal extract. It is better, however, to add excess of hydrochloric acid to the ammoniacal extract and then precipitate by saturation with sulphuretted hydrogen; any arsenic originally present as As_2S_3 naturally comes down before passing in the gas. The arsenic

[1] *J. Soc. Chem. Ind.*, 1902, 21, 832. [2] *Pharm. Centr.*, 1884, 265 and 443.

present is best estimated by Schäppi's method,[1] which consists in exactly neutralising the ammoniacal solution with nitric acid, diluting, and then titrating with $N/10$ silver nitrate solution, using as indicator neutral potassium chromate, which is coloured brown by a drop of the solution after all the arsenic has been precipitated.

The salts of arsenious acid remain in the insoluble residue on extracting sulphur with carbon bisulphide; this residue must be digested with aqua regia and examined for arsenic in the usual manner, as is described more fully under "Sulphuric Acid" (p. 433 *et seq.*).

5. **Selenium** may be detected by oxidising the sulphur, best by deflagrating with nitre; on dissolving the melt in hydrochloric acid and treating with sulphurous acid, selenium will, if present, be precipitated as a red powder.

In America, according to Reed,[2] the examination for selenium is carried out as follows:—0·5 g. of the sulphur is boiled with a solution of 0·5 g. potassium cyanide in 5 c.c. of water, the solution filtered, and the filtrate acidified with hydrochloric acid; after standing for an hour no red coloration due to selenium should result. A pale yellow coloration, due to perthiocyanic acid, may be neglected. The test is made still more sensitive by boiling 1 g. of the sulphur for an hour with a solution of 2 g. of potassium cyanide, then adding a further 0·5 g. potassium cyanide and continuing the boiling for half an hour. Any iron present will, of course, react with the thiocyanate formed.

For methods of determining minute amounts of selenium in sulphur or pyrites, see Klason and Mellquist[3] and Smith.[4]

6. **Determination of Sulphur**.—Macagno[5] recommends the direct method of extraction with carbon bisulphide, and has calculated a table for this purpose. The method has been investigated by Pfeiffer[6] and the specific gravities involved determined with considerable exactitude. To estimate sulphur by this process, a weighed quantity of the powdered sample is shaken in a well-stoppered bottle with at least four times its weight of pure carbon bisulphide, accurately weighed, and the specific gravity of a clear sample determined at a known temperature (+15° C. and higher).

The specific gravity thus determined is if necessary reduced to that at 15° C. by means of the formula:

$$\text{Specific gravity at } 15^\circ = \text{spec. grav. at } t^\circ \times \frac{1 + at + bt^2 + \ .\ \ .}{1 + a \times 15 + b \times 15^2}$$

where $a = 0{\cdot}0011398$ and $b = 0{\cdot}000001370$.

[1] *Chem. Ind.*, 1881, **4**, 409.

[2] *Chem. Zeit. Rep.*, 1897, **21**, 252.

[3] *Z. angew. Chem.*, 1912, **25**, 514; *J. Soc. Chem. Ind.*, 1912, **31**, 331.

[4] *J. Ind. Eng. Chem.*, 1915, **7**, 849; *J. Soc. Chem. Ind.*, 1915, **34**, 1090.

[5] *Chem. News*, 1881, **43**, 192.

[6] *Z. anorg. Chem.*, 1897, **15**, 194; also, P. Fuchs, *Z. angew. Chem.*, 1898, **11**, 1189.

The percentage of pure sulphur in the sample examined is deduced from the formula:

$$\% S = \frac{a \times b}{c},$$

where—

a = the weight of sulphur dissolved by 100 g. carbon bisulphide, according to the following table,

b = the weight of carbon bisulphide used in the extraction,

c = the weight of substance.

Specific gravities of solutions of Sulphur in Carbon Bisulphide with the corresponding weights of Sulphur dissolved by 100 parts by weight of pure Carbon Bisulphide at 15° C., compared with Water at 4° C.

Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.
1·2708	0·0	1·2999	6·4	1·3263	12·8	1·3507	19·2
1·2717	0·2	1·3007	6·6	1·3271	13·0	1·3514	19·4
1·2726	0·4	1·3016	6·8	1·3279	13·2	1·3521	19·6
1·2736	0·6	1·3024	7·0	1·3287	13·4	1·3529	19·8
1·2745	0·8	1·3032	7·2	1·3295	13·6	1·3536	20·0
1·2754	1·0	1·3041	7·4	1·3303	13·8	1·3543	20·2
1·2763	1·2	1·3050	7·6	1·3311	14·0	1·3550	20·4
1·2772	1·4	1·3058	7·8	1·3319	14·2	1·3557	20·6
1·2782	1·6	1·3066	8·0	1·3326	14·4	1·3564	20·8
1·2791	1·8	1·3074	8·2	1·3334	14·6	1·3571	21·0
1·2800	2·0	1·3083	8·4	1·3342	14·8	1·3577	21·2
1·2809	2·2	1·3091	8·6	1·3350	15·0	1·3584	21·4
1·2819	2·4	1·3100	8·8	1·3357	15·2	1·3591	21·6
1·2828	2·6	1·3108	9·0	1·3365	15·4	1·3598	21·8
1·2838	2·8	1·3116	9·2	1·3373	15·6	1·3605	22·0
1·2847	3·0	1·3125	9·4	1·3380	15·8	1·3612	22·2
1·2856	3·2	1·3133	9·6	1·3388	16·0	1·3619	22·4
1·2866	3·4	1·3142	9·8	1·3396	16·2	1·3626	22·6
1·2875	3·6	1·3150	10·0	1·3403	16·4	1·3633	22·8
1·2885	3·8	1·3158	10·2	1·3411	16·6	1·3640	23·0
1·2894	4·0	1·3166	10·4	1·3418	16·8	1·3646	23·2
1·2903	4·2	1·3174	10·6	1·3426	17·0	1·3653	23·4
1·2912	4·4	1·3182	10·8	1·3433	17·2	1·3660	23·6
1·2920	4·6	1·3190	11·0	1·3441	17·4	1·3667	23·8
1·2929	4·8	1·3199	11·2	1·3448	17·6	1·3674	24·0
1·2938	5·0	1·3207	11·4	1·3456	17·8	1·3681	24·2
1·2947	5·2	1·3215	11·6	1·3463	18·0	1·3688	24·4
1·2956	5·4	1·3223	11·8	1·3470	18·2	1·3695	24·6
1·2964	5·6	1·3231	12·0	1·3478	18·4	1·3702	24·8
1·2973	5·8	1·3239	12·2	1·3485	18·6	1·3709	25·0
1·2982	6·0	1·3247	12·4	1·3492	18·8	...	...
1·2990	6·2	1·3255	12·6	1·3500	19·0	...	...

Bruno[1] determines total sulphur as follows:—1 g. is boiled for twenty minutes with 10 c.c. of sodium hydroxide solution (sp. gr. 1·33) and 20 c.c. of water. The solution is cooled, made up to 100 c.c., filtered through a dry filter, and 25 c.c. boiled with five successive quantities

[1] *Ann. Falsif.*, 1910, 3, 129; *J. Soc. Chem. Ind.*, 1910, 29, 626.

of 5 c.c. each of a solution consisting of 10 c.c. of the same sodium hydroxide solution, 2 c.c. of bromine, and 20 c.c. of water. The solution is then acidified with hydrochloric acid, the excess bromine expelled by boiling, and the sulphur determined as barium sulphate.

In regard to the examination of refined sulphur—

Roll Sulphur is generally to all intents chemically pure; it may be examined for ash, arsenic, and selenium (see pp. 360-362).

Flowers of Sulphur are not quite so pure; if not carefully washed, they are especially liable to contain free acid, more particularly sulphurous acid, sulphuric acid, and also thiosulphuric acid, which may be tested for by the usual methods. If intended for use in the manufacture of fireworks, the sulphur must be free from all trace of acidity. According to determinations made by Janda,[1] the residue on ignition amounted to 0·063 per cent. as an average of thirty samples, the maximum value being 0·283 per cent. The solubility in boiling sodium hydroxide solution of 1·2 sp. gr. led to a mean value of 98·04 per cent., with a maximum of 99·99 per cent., and a minimum of 88 per cent.; in one case, however, only 68 per cent. was dissolved.

According to Domergue,[2] only those products should be classed as "flowers of sulphur" which, when fresh, contain at least 33 per cent. insoluble in carbon bisulphide.

On the analysis of sulphur, see further Taurel and Griffet,[3] Levi,[4] Wentzel,[5] and Wolff.[6]

II. Sulphur from Gas Residuals

The spent purifying materials from gasworks frequently contain over 50 per cent. of free sulphur.[7] They are first freed from ammonium salts by extraction with water, and then subjected to a special treatment for the recovery of cyanogen compounds (see p. 650 *et seq.*). The residue remaining after this treatment forms a valuable raw material for the production of sulphurous acid. It consists essentially of free sulphur and oxide of iron admixed with sawdust, tarry substances, etc., and may also contain varying quantities of lime, etc. Any lime present will, on burning, fix part of the sulphur, and on this account a method of analysis is adopted which takes account of available sulphur only.[8] The spent oxide is burnt by the aid of platinised asbestos, the resulting

[1] *Jahresber. d. chem. Tech.*, 1897, 421. [2] *Chem. Zeit. Rep.*, 1905, **29**, 19.

[3] *Comptes rend.*, 1911, **152**, 1182; *J. Soc. Chem. Ind.*, 1911, **30**, 683.

[4] *Annali Chim. Appl.*, 1915, **1**, 9; *J. Soc. Chim. Ind.*, 1915, **34**, 282.

[5] *Z. angew. Chem.*, 1918, **31**, 78. [6] *Ibid.*, 128.

[7] The examination of these residuals for their more important constituents will be described in the section on Gas Manufacture, Vol. IV.

[8] Zulkowsky, *Dingl. polyt. J.*, 1881, **241**, 52.

gases are passed into a solution of potassium hydroxide and potassium hypobromite, and the sulphuric acid contained in the resulting solution estimated by precipitation with barium chloride.

The burning is effected in a combustion tube, 60 cm. in length (Fig. 187), narrowed at *a*, and drawn out at one end into a downwardly directed and not too thin narrower piece 10 cm. long. A layer of platinised asbestos, 20 to 25 cm. long, is placed between *a* and *b*, and 7 to 10 cm. behind this a porcelain boat containing about 0·4 g. of the sulphur. The free end of the tube is connected at *k* with a gasholder containing oxygen. Two 14 cm. high bulb U-tubes *c* and *d* and the tube *e*, filled with glass wool, are employed for absorbing the evolved gases. They are charged with a solution prepared by dissolving 180 g. of potassium hydroxide (purified from sulphate by alcohol) in water, adding to this 100 g. of bromine drop by drop, cooling as required, and diluting to 1 litre; thirty c.c. of this solution is sufficient for

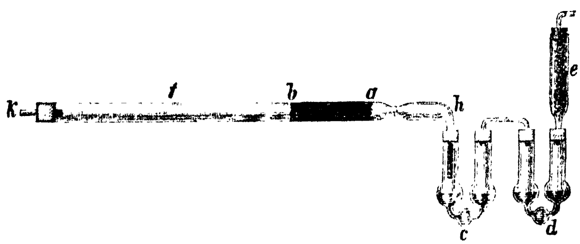

FIG. 187.

the estimation of 0·5 g. sulphur. The glass wool in the tube *e* should also be moistened with the solution.

A current of moist oxygen is passed through the tube, and the portion between *a* and *b* heated to redness; the boat is then pushed in and the heating extended from right to left, until finally the tube is heated to the point *f*. The current of gas must be much more rapid than that employed in ordinary organic combustions, in order to prevent sulphur from passing away unburnt; on the other hand, it must not be so strong that the sulphur dioxide escapes unabsorbed. Any deposit formed at *h* must be driven forward by means of a Bunsen burner; the combustion is complete when such deposit ceases to form, and this is usually the case after one hour. The absorbing vessels are then removed, emptied, and washed out; any sulphuric acid remaining in the tube at *h* is recovered by repeatedly drawing up water by suction applied at *k*. The solutions and washings are combined, hydrochloric acid added in sufficient excess to neutralise the alkali and decompose the hypobromite, the whole heated and if necessary concentrated, and the sulphuric acid precipitated as barium sulphate by addition of a hot solution of barium chloride.

This method is also applicable to the determination of available sulphur in pyrites; in this case the platinised asbestos is omitted, and the combustion tube, drawn out and bent round as above, need not be more than 40 cm. long.

Hydrogen peroxide may be used with advantage instead of potassium hypobromite solution, titration of the sulphuric acid by standard alkali being substituted for the gravimetric determination. Allowance must, of course, be made for any acidity in the hydrogen peroxide employed. This modification is much more rapid than Zulkowsky's method, and does away with the necessity of employing absolutely sulphate-free potassium hydroxide. The reaction is simple:

$$H_2O_2 + SO_2 = H_2SO_4.$$

Similar methods, generally intended for the determination of available sulphur in pyrites, have frequently been recommended; these are described below.

The determination of the sulphur by oxidation with hydrogen peroxide always gives too high results, and some tar is also dissolved.

Pfeiffer[1] burns 1 g. of the sample in a bottle filled with oxygen, on the bottom of which a solution of sodium hydroxide is placed. The solution is finally oxidised with 1 c.c. of 30 per cent. neutral hydrogen peroxide, and titrated.

III. PYRITES[2] (and other Metallic Sulphides)

Pyrites is generally received in sealed duplicate samples of 200 to 300 g., the average sample being prepared according to the rules given on p. 8.

The most important determination for the acid manufacturer is naturally that of the sulphur content. In addition, moisture, and less frequently copper, arsenic, zinc, and carbonates are determined. The complete analysis of pyrites is very seldom undertaken, generally only in examining the first consignments from a new source.

1. Moisture.—The coarsely ground sample is dried at 105°, until the weight becomes constant. For the following tests, the finely divided average sample preserved in a well-sealed bottle, not the dried sample, is employed.

The analytical results are calculated on the dry pyrites, for which reason a special moisture determination in the average sample is necessary.

2. Sulphur.—It must be decided whether the total sulphur, or that rendered soluble by aqua regia, or finally that recoverable by heating

[1] *J. Gasbeleucht.*, 1905, 48, 977; *Chem. Centr.*, 1905, II., 1831.

[2] *Cf.* W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, 1923, p. 68.

in a current of air, is to be determined. Sulphur present as heavy spar or galena would be included in the first case, which is useless for the production of sulphurous acid. For this reason and also because of its greater rapidity, and the avoidance of the fusion, which strongly attacks the platinum crucible, the wet method, as recommended by Lunge,[1] is almost universally used. By publication in the *Alkali Makers' Handbook* the method has attained the rank of a standard process, and is generally employed in buying and selling.

The third group of methods in which the available sulphur is estimated has been dealt with under "Gas Residuals" (p. 364); it is not as a rule employed for pyrites.

As a preliminary to any method of determination it is essential to reduce the sample to a very fine powder, first in a steel mortar and finally in an agate mortar. A porcelain or Wedgwood mortar should not be used, as they yield quite appreciable quantities of foreign matter to the sample. The complete sample is then sifted through very fine silk gauze, without elimination of any residue.

Lunge's method for the wet extraction of pyrites is as follows:—0·5 g. of the pyrites is treated with about 10 c.c. of a mixture of 3 volumes nitric acid of 1·4 sp. gr. and 1 volume strong hydrochloric acid (both acids must be tested for complete freedom from sulphuric acid), with occasional heating, and care being taken to avoid spurting (*cf.* p. 16). In exceptional cases some free sulphur may separate; if so, it may be oxidised by the cautious addition of potassium chlorate. The mixture is evaporated to dryness on the water-bath and this evaporation is repeated after the addition of 5 c.c. of hydrochloric acid, after which nitrous fumes should cease to be evolved. A further 1 c.c. of concentrated hydrochloric acid is added to the residue on the water-bath, and after a few minutes 100 c.c. of hot water is added, the whole filtered through a small filter paper and the insoluble matter washed with hot water.[2] The residue may be dried, ignited, and weighed. It may contain in addition to silica and silicates, barium, lead, and occasionally calcium sulphates, the sulphuric acid of which being absolutely non-available is purposely neglected. If the residue is not to be estimated, the filtration may be neglected and the precipitation with ammonia proceeded with as soon as all the nitric acid has been driven off.

To remove the iron, the filtrate and washings are neutralised with ammonia, an excess of 5 to 7 c.c. of strong ammonia solution is added, and the liquid heated to 60° and 70° for ten to fifteen minutes, but

[1] *Z. anal. Chem.*, 1881, **20**, 419; and *Z. angew. Chem.*, 1889, **2**, 473. Pattinson, *J. Soc. Chem. Ind.*, 1905, **24**, 9; *cf.* Treadwell, *Analytical Chemistry*, 5th edition, vol. ii., p. 467.

[2] *Cf.* Dennstedt and Hassler, *Z. angew. Chem.*, 1905, **18**, 1137 and 1562; also, G. Lunge, *ibid.*, 1905, **18**, 1656.

the solution should not be heated to boiling; it should still smell strongly of ammonia, otherwise the precipitate may contain basic ferric sulphate.

The separated ferric hydroxide is filtered off and washed. The operation may be carried out in shorter time (one-half to one hour) by observing the following precautions:—1. Filtering hot and washing on the filter with hot water, taking care to avoid channels by thoroughly disturbing the whole precipitate with each washing. 2. Using a sufficiently dense but rapid filtering paper. 3. Employing a correctly made funnel with an angle of 60°, the tube of which fills completely with the filtrate.

The washing is continued until about 1 c.c. of the washings yields no turbidity with barium chloride after standing several minutes. In doubtful cases it is advisable to prove the complete absence of basic sulphate by fusing the dried ferric hydroxide precipitate with pure sodium carbonate and examining the aqueous extract of the melt for sulphuric acid.

Hundreds of check tests, carried out in the manner described, have shown (Lunge) that by observing the above precautions even novices almost always obtain a ferric hydroxide free from sulphuric acid, and that with experienced workers this is always the case. Küster and Thiel,[1] who incorrectly assume that the ferric hydroxide cannot be completely freed from sulphuric acid by washing, recommend as an alternative method to precipitate with barium chloride without previous removal of the ferric hydroxide but to remove this subsequently by prolonged digestion with hydrochloric acid, or to add a considerable amount of ammonium oxalate so as to prevent altogether the precipitation of the iron. Both methods occupy much more time than that described above and are in no way more exact.[2]

The combined filtrate and washings should not exceed 300 c.c.; if they do they must be concentrated by evaporation. The solution is acidified with pure hydrochloric acid, avoiding any considerable excess, heated to distinct boiling, and after removal of the flame a solution of barium chloride, also at the boiling temperature, added all at once with constant stirring. By adding the hot barium chloride solution all at once to the solution to be precipitated, instead of drop by drop, an error is introduced owing to the absorption of some barium chloride by the barium sulphate, but this just compensates the loss caused by the solubility of the barium sulphate in the solution, and the error due to the unavoidable co-precipitation of double sulphates of barium and ammonium. The presence of copper introduces no error in the de-

[1] *Z. anorg. Chem.*, 1899, **19**, 97; 1900, **22**, 424.

[2] *Cf.* Lunge, *Z. anorg. Chem.*, 1899, **19**, 454; Herting, *Z. angew. Chem.*, 1899, **12**, 274; also, *Chem. Zeit.*, 1899, **23**, 768.

termination; zinc if present in small quantities has also no effect, but if present in larger proportions, as in the analysis of blende, the error is greater, owing to the solubility of barium sulphate in the ammonium salts necessary to keep the zinc in solution. This error is, however, also compensated, as stated above, by adding the barium chloride solution all at once.[1] Twenty c.c. of a 10 per cent. barium chloride solution diluted with 100 c.c. of water, will suffice for ½ g. of pyrites. A larger excess of barium chloride is to be avoided, or the results will come out too high. The whole is allowed to stand for forty minutes after precipitating, by which time the filtrate should have cleared completely and be ready for further treatment. The clear liquid is decanted as completely as possible through a filter, 100 c.c. of boiling water poured on to the precipitate and the whole stirred; after two to three minutes the solution should have cleared again and be ready for a further decantation. The washing by decantation is repeated three or four times until the liquid ceases to show an acid reaction; the precipitate is then washed on the filter, dried and ignited. It should be perfectly white and should not cake. The filter paper, after separating the precipitate, is either burnt in a platinum spiral, or the filter paper and precipitate are burnt wet in the crucible. In the latter case it is necessary to convert the resulting barium sulphide into sulphate, by gentle ignition with the crucible in a slanting position. One part $BaSO_4 = 0{\cdot}1373$ parts of sulphur.

With practice, the total volume of solution to be precipitated with barium chloride will not exceed 300 c.c., so that evaporation, before precipitating, should not be necessary. If it is unavoidable it must be carried out on the water-bath, or in such manner that any sulphurous combustion products are kept away from the solution, *e.g.* by heating on an asbestos or aluminium plate.

Other methods for removing the iron are described by Heidenreich,[2] by Herting and Lehnhardt,[3] by Gyzander,[4] and by Smoot.[5]

The previous precipitation of the iron is necessary, since, if present, it gives rise to the formation of a double sulphate of iron and barium in the barium precipitate, which double sulphate loses part of its sulphuric acid on ignition.[6] The resulting error may, according to Lunge, reach a maximum of ½ per cent. in the case of pyrites (this result differing from that of Thiel, who lost up to 7 per cent.); it is, however, avoided by precipitating the iron as described on pp. 367-368.

[1] Lunge and Stierlin, *Z. angew. Chem.*, 1905, **18**, 1921.
[2] *Z. anorg. Chem.*, 1899, **20**, 233.
[3] *Chem. Zeit.*, 1899, **23**, 768.
[4] *Chem. News*, 1906, **93**, 213.
[5] *Eng. and Min. J.*, 1912, **94**, 412; *J. Soc. Chem. Ind.*, 1912, **31**, 918.
[6] *Cf.* Jannasch and Richards, *J. prakt. Chem.*, 1889, **39**, 321; also, correction by these authors in consequence of communication from Lunge, *ibid.*, 1889, **40**, 236. See also Lunge, *Z. angew. Chem.*, 1889, **12**, 473.

The injurious effect of a large excess of barium chloride, owing to absorption by the barium sulphate precipitate, has long been known, and Lunge has drawn special attention to this point. Richards and Parker[1] have carefully investigated the subject, but the methods of purification suggested by them, in addition to being extremely troublesome, fail in their purpose unless the solubility of barium sulphate in the solution in which precipitation occurs be taken into account. Richards states that under ordinary conditions the two errors exactly compensate each other, and a result very near the truth may consequently be expected if the details given above are carefully followed.

Allen and Bishop[2] have devised a method which, slightly altered after co-operative work, has been widely adopted by American chemists. The modified method is as follows:[3]—0·5495 g. of the powdered sample, dried at 100° C., is treated with 6 to 8 c.c. of a mixture of two parts of bromine and three parts of carbon tetrachloride by volume, and left for fifteen minutes in a tall covered beaker, with occasional shaking. 10 c.c. of concentrated nitric acid is then added, and after standing for fifteen minutes, with occasional shaking, the mixture is heated below 100° until most of the bromine has been expelled, and then evaporated to dryness on a steam plate. The residue is treated with 10 c.c. of concentrated hydrochloric acid, the mixture evaporated to dryness, and the residue heated at 100° for half to one hour to dehydrate the silica, then moistened with 1 c.c. of concentrated hydrochloric acid and heated with 50 c.c. or more of water until solution is complete. After cooling for three to five minutes, 0·1 g. of powdered aluminium is added, and when reduction of the iron is complete the solution is filtered, and the residue washed nine times with hot water. The solution is treated with 2·5 c.c. of concentrated hydrochloric acid, then diluted to 650 c.c. and 50 c.c. of cold 5 per cent. barium chloride solution added slowly, without stirring, preferably in single drops at the rate of about 5 c.c. per minute. The mixture is stirred, allowed to stand for at least two hours, and the precipitate collected on a thick layer of asbestos in a Gooch crucible, using suction. After washing with cold water, the precipitate is dried and ignited. According to the authors, no correction for the presence of occluded salts in the barium sulphate is necessary. The results are accurate, and duplicate determinations are always very closely concordant.

Such methods as solution of the pyrites in fuming nitric acid, or in hydrochloric acid and potassium chlorate or sodium chlorate,[4] or in

[1] *Z. anorg. Chem.*, 1895, 8, 413.

[2] *Eighth Int. Congr. Appl. Chem.*, 1912. Section I., Orig. Comm., 1, 33; *J. Soc. Chem. Ind.*, 1912, 31, 919.

[3] H. C. Moore, *J. Ind. Eng. Chem.*, 1916, 8, 1167; *J. Soc. Chem. Ind.*, 1917, 36, 29.

[4] Noaillon, *Z. angew. Chem.*, 1897, 10, 351.

hydrochloric acid saturated with bromine, are less satisfactory than that described above, owing to the liability of the sulphur to separate.

For other investigations into the conditions of precipitation of barium sulphate, see Sacher,[1] Van't Kruys,[2] Allen and Johnston,[3] Gooch and Hill,[4] Karaoglanow.[5]

Of the dry methods of analysis, that of Fresenius,[6] though somewhat tedious, is probably the most exact. 0·5 g. of pyrites is fused with 10 g. of a mixture composed of two parts of sodium carbonate and one part of potassium nitrate, the melt is extracted with water, and after precipitation of the lead by a slow current of carbonic anhydride, the solution is boiled with sodium carbonate solution, filtered, and the residue washed with hot water. The combined filtrate and washings are acidified with hydrochloric acid, evaporated several times with additions of hydrochloric acid to remove the nitric acid, the residue taken up with dilute hydrochloric acid and precipitated by barium chloride, the barium sulphate precipitate after ignition being finally purified by boiling with hydrochloric acid. This is a lengthy process, and has been replaced by Lunge's method even in Fresenius' laboratory.

Other dry methods are generally restricted to the determination of sulphur in burnt ore (see p. 389), to a preliminary testing of iron pyrites, or to the analysis of some special pyrites for which the wet method is less suitable. The wet method is always the best for pyrites, containing only about 4 per cent. of copper, *e.g.*, Spanish pyrites. The method used in Freiberg is to heat 1 g. of powdered pyrites to a red heat in a muffle furnace with 2 g. of sodium carbonate and 2 g. of potassium nitrate; the melt is extracted with hot water, filtered into excess of hydrochloric acid, and titrated with barium chloride solution by Wildenstein's method (*cf.* p. 373).

The best dry methods of treatment appear to be those in which sodium peroxide is employed, as, for example, those recommended by Hempel and by Höhnel and Glaser.[7] List[8] recommends the following simplification of a method proposed by Fournier:—0·5 g. of the finely divided pyrites (or burnt ore) is intimately mixed with 5 to 6 g. of powdered sodium peroxide in a wrought-iron crucible, which is then covered and gently heated in a Bunsen flame. Reaction quickly sets in and is complete in one minute. As soon as the mass is fused the flame is removed and the crucible plunged into 150 to 200 c.c. of warm water, in

[1] *Chem. Zeit.*, 1909, **33**, 941; *J. Soc. Chem. Ind.*, 1909, **28**, 1066.
[2] *Chem. Weekblad*, 1909, **6**, 735; *Analyst*, 1910, **35**, 374.
[3] *J. Amer. Chem. Soc.*, 1910, **32**, 588, and *J. Ind. Eng. Chem.*, 1910, **2**, 196; *Analyst*, 1910, **35**, 331 and 332.
[4] *Z. anorg. Chem.*, 1913, **80**, 397; *Analyst*, 1913, **38**, 339.
[5] *Z. anal. Chem.*, 1917, **56**, 417, 487, 561; *J. Soc. Chem. Ind.*, 1918, **37**, 109 A, 168 A, 204 A.
[6] *Z. anal. Chem.*, 1877, **16**, 335.
[7] *Chem. Zeit.*, 1894, **18**, 1448.
[8] *Z. angew. Chem.*, 1903, **16**, 414.

which the melt quickly dissolves. The contents of the crucible are washed out and the solution approximately neutralised with 10 c.c. concentrated hydrochloric acid, filtered from the insoluble ferric hydroxide, which is washed as recommended on p. 368, and the barium sulphate precipitated as there described. List states that in absence of sulphate of lead or of alkaline earth metals, the results agree with those obtained by Lunge's wet method. The iron crucibles are cheap and will stand fifty fusions.

Clark[1] heats with sodium bicarbonate and magnesia, and estimates the resulting sulphuric acid gravimetrically. Fahlberg and Iles[2] fuse with a large excess of potassium hydroxide in a silver crucible.

Of methods intended for the estimation of *available sulphur*, that is, of such sulphur as is converted into sulphur dioxide on roasting, that of Zulkowsky has been described under Gas Residuals (p. 364). Similar methods have been previously described by Mixter,[3] Brügelmann,[4] Sauer,[5] and Jannasch.[6] These methods have not been adopted in general practice for the examination of iron pyrites; they are, however, useful in the case of mixed pyrites and the like.

Silberberger[7] has proposed to replace barium chloride in the gravimetric method by precipitating the sulphuric acid in alcoholic solution with strontium chloride. This suggestion has been opposed by Lunge,[8] and the method has been rejected by the Analysis Committee of the International Congress of Applied Chemistry.[9]

Numerous proposals have been made to shorten the determination of fixed sulphuric acid by employing a volumetric method. Such methods, however, in spite of the contrary view of Teschemacher and Smith,[10] do not possess the exactness of the gravimetric determination, and further, the saving of time, unless many determinations are made simultaneously, is not considerable. At the same time it is to be borne in mind that the gravimetric determination of sulphuric acid as barium sulphate is by no means one of the most exact analytical operations, and may, in spite of all precautions, give an error amounting to $\frac{1}{200}$ of the whole, or many times that involved in the determination of chlorine as silver chloride.

The more important volumetric methods for the determination of fixed sulphuric acid are appended, although, as stated, they are not sufficiently accurate to justify their use in the case of pyrites.

Wildenstein[11] titrates with a normal solution of barium chloride, and

[1] *J. Soc. Chem. Ind.*, 1885, 4, 329 and 724.
[2] *Ber.*, 1878, 11, 1187.
[3] *Amer. Chem. J.*, 1880-81, 2, 396.
[4] *Z. anal. Chem.*, 1873, 12, 32.
[5] *Ibid.*, 1876, 15, 175.
[6] *J. prakt. Chem.*, 1889, 40, 239; 1890, 41, 566.
[7] *Ber.*, 1903, 36, 2755, 4259.
[8] *Ber.*, 1903, 36, 3387. *Z. angew. Chem.*, 1904, 17, 913, 949; 1905, 18, 449.
[9] *Report*, 1906, p. 344.
[10] *Chem. News*, 1871, 24, 61, 66, and 140.
[11] *Z. anal. Chem.*, 1862, 1, 432. See also H. T. Bucherer, *Z. anal. Chem.*, 1920, 59, 297.

determines the end-point by testing a small filtered sample as follows:— The solution is placed in an inverted bell-jar A (Fig. 188), through the neck of which passes a bent tube *b*, which is closed below by a spring clip *z* and ends above in a funnel *f* bent downwards, which is closed with two thicknesses of filter paper covered and held in position with muslin. The level of acidified solution must extend above the funnel. The barium chloride solution is run into this with good stirring, and after each addition a filtered sample is withdrawn by first allowing several c.c. to flow through *f* and pouring them back into A, and then drawing a further sample and testing this with a drop of barium chloride solution. If a precipitate results, the sample is poured back into A, more barium chloride added, and a further test made. Should the end-point be overstepped, a few c.c. of normal sulphuric acid are added to the solution and the testing completed, the volume of acid added being subtracted from the volume of barium chloride used.

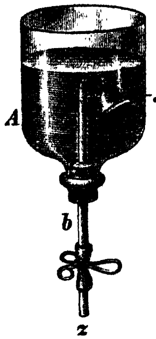

FIG. 188.

Wilsing[1] exactly neutralises the sulphate solution, using phenolphthalein as indicator, heats to boiling in a porcelain dish, and adds a measured quantity of a 4 per cent. barium chloride solution together with phenolphthalein, and then titrates with a 2 per cent. solution of sodium carbonate until the red coloration is obtained. The volume of carbonate solution required gives the excess of barium chloride added.

Similar methods have been described by Carl Mohr,[2] Knöpfler,[3] Monhaupt,[4] Blacher and Koerber,[5] Tarugi and Bianchi,[6] and others.

Andrews[7] precipitates the sulphuric acid by adding excess of a hydrochloric acid solution of barium chromate to the boiling solution of the sulphate; the excess of the precipitating reagent is removed by addition of ammonia or of calcium carbonate to the boiling solution, the whole filtered, and washed with hot water. The filtrate, which contains alkali chromate corresponding to the sulphate originally present, is cooled, concentrated hydrochloric acid added, followed by potassium iodide, and the liberated iodine titrated with sodium thiosulphate. According to Reuter,[8] only 5 c.c. of concentrated hydrochloric acid should be added, the whole washed for five minutes after the addition of the potassium iodide, the beaker being kept covered and a current of carbon dioxide passed over the surface of the solution.

Mitchell and Smith[9] add to the solution of the sulphate a measured

[1] *Chem. Ind.*, 1886, **9**, 25.
[2] *Annalen*, 1854, **90**, 165.
[3] *Ibid.*, 1885, **230**, 260.
[4] *Chem. Centr.*, 1905, **I.**, 296.
[5] *Ibid.*, 1905, **II.**, 511.
[6] *Gazz. Chim. Ital.*, 1906, **36**, 347.
[7] *Chem. Zeit. Rep.*, 1889, **13**, 39.
[8] *Chem. Zeit.*, 1898, **22**, 357.
[9] *J. Chem. Soc.*, 1909, **95**, 2198; *J. Soc. Chem. Ind.*, 1910, **29**, 47.

amount (in slight excess) of $2N/5$ barium chloride solution. The solution is boiled, neutralised by ammonia, sodium acetate and acetic acid are added, then a measured volume of $N/10$ ammonium bichromate. After cooling, the solution is made up to a known volume, and an aliquot part titrated with $N/10$ ferrous ammonium sulphate (potassium iodide and thiosulphate could be used instead), to determine the excess of chromate. Results are accurate; but with potassium sulphate there is considerable adsorption, and the barium sulphate precipitate must be boiled for some hours with dilute hydrochloric acid before neutralising with ammonia and proceeding as above. (*Note.*—Ammonium bichromate, which as an oxidiser is $N/10$, is only $N/30$ as a precipitant.)

For other modifications of the chromate method, see Marboutin and Moulinié,[1] Telle,[2] Holliger,[3] and Roemer;[4] for other volumetric methods see Grossmann,[5] Nikaido,[6] and Riegler.[7]

The methods first proposed by Vaubel,[8] and based on the use of benzidine, have attracted attention. W. A. Müller[9] has found that fixed sulphuric acid can be quantitatively precipitated by benzidine hydrochloride when the latter is present in sufficient excess, and that such excess can be directly determined by titration with alkali. This is due to benzidine being such a very weak base, that the hydrochloride is sufficiently dissociated hydrolytically in solution to behave like free hydrochloric acid towards phenolphthalein. The decomposition corresponds to the equation:—

$$R_2SO_4 + C_{12}H_{12}N_2 . 2HCl = 2RCl + C_{12}H_{12}N_2 . H_2SO_4.$$

Raschig[10] has modified Müller's method as follows. Forty g. of benzidine is ground up with 40 c.c. of water, washed with about 750 c.c. of water into a litre flask, 50 c.c. of concentrated hydrochloric acid added, and then water to the graduation mark. On shaking, the whole or the greater part dissolves to a brown solution, which is filtered if necessary, and then diluted to twenty times its volume. One hundred and fifty c.c. of this weak solution is used to precipitate 0·1 g. sulphuric acid. The sulphate solution to be examined is allowed to flow, with continual stirring, into the benzidine solution, and the benzidine sulphate which rapidly separates is filtered off at the pump. A 200 c.c. funnel, fitted with a Witt's filter plate, is used for the filtration. The plate, which is of 40 mm. upper diameter, is covered by two moistened filter papers

[1] *Chem. Centr.*, 1898, I., 218. [2] *Ibid.*, 793.
[3] *Z. anal. Chem.*, 1910, 49, 84; *J. Soc. Chem. Ind.*, 1910, 29, 455.
[4] *Ibid.*, 490; *J. Soc. Chem. Ind.*, 1910, 29, 902.
[5] *Chem. News*, 1880, 41, 114; *Ber.*, 1880, 13, 824.
[6] *J. Amer. Chem. Soc.*, 1902, 24, 774. [7] *Z. anal. Chem.*, 1902, 41, 17.
[8] *Ibid.*, 1896, 35, 821. [9] *Ber.*, 1902, 35, 1587.
[10] *Z. angew. Chem.*, 1903, 16, 617 and 818.

of 46 mm. diameter, the extending edges of which are, after applying the suction, pressed by means of a sharp-angled glass rod to form a circular pad, and so make the filter perfectly tight. Any precipitate adhering to the walls of the beaker or other vessel used for the precipitation is washed off with a portion of the clear filtrate, and as the last drop of mother liquor drains off from the filter, the precipitate is washed twice successively with from 5 to 10 c.c. of water. By thus washing with a minimum quantity of water, the objection raised by W. A. Müller and others to the method on the ground of the solubility of benzidine sulphate in the wash-water is overcome. The funnel is removed from the filter-flask, placed on a watch-glass of 50 to 60 mm. diameter, inverted, the filter-plate and precipitate transferred to the watch-glass by the aid of a glass rod, the filter-plate removed, the filter pressed together in the fingers and dropped into an Erlenmeyer flask of 250 c.c. capacity and 30 mm. wide at the neck. The watch-glass and funnel are washed with not more than 25 c.c. of water, and the washings added to the contents of the flask, which is then closed with a rubber stopper and well shaken until there results a uniform magma of precipitate and disintegrated filter paper quite free from small lumps of benzidine sulphate. The mixture is then warmed to 50°, and after addition of phenolphthalein titrated with $N/10$ sodium hydroxide solution, finally heating to boiling to remove from the solution all carbon dioxide, since it affects the indicator. An accidental excess of alkali solution may be titrated back with normal acid. This method is applicable to the estimation of sulphuric acid present either in the free state or as copper or ferrous sulphate; it is not directly applicable to ferric sulphate, as in this case the iron must be precipitated as described on pp. 367-368. The method is also inapplicable in many other cases, for example in the presence of certain organic compounds.

The benzidine method may, moreover, be used even in the presence of iron when not more than 1 atom of sulphur is present per atom of iron, provided that (as first recommended by M. Schlötter) ferric salts are first reduced to the ferrous state. For this purpose, Raschig[1] employs a dilute solution of hydroxylamine hydrochloride, and gives the following details for the determination of sulphur in pyrites by this method. Exactly 0·8 g. of the finely divided sample is weighed into a 200 c.c. conical flask, 5 c.c. of fuming nitric acid added, and the flask with a small funnel in the neck heated on the water-bath. After half an hour, 30 c.c. of water is added, the whole of the contents rinsed into a 100 c.c. flask, made up to the mark and well shaken. Twenty c.c. of this solution is then placed in a 600 c.c. beaker, 10 c.c. of a 1 per cent. solution of hydroxylamine hydrochloride added, and 500

[1] *Z. angew. Chem.*, 1905, **18**, 331; 1906, **19**, 331.

c.c. of benzidine hydrochloride solution prepared as above. The precipitation and subsequent treatment of the benzidine sulphate is then carried out as described. The filtrate from the sulphate should always be tested with barium chloride, to make sure that sufficient benzidine solution has been used for complete precipitation.

For further investigations on this method, see also von Knorre.[1]

3. **Arsenic.**—The estimation of arsenic in pyrites is somewhat laborious, and is consequently not carried out in works as frequently as its importance would demand. The arsenic in pyrites not only finds its way into the vitriol, but also into the hydrochloric acid prepared therefrom, and may, in this and in many other cases, prove very harmful. The methods employed for its determination unfortunately lead to widely differing results.

According to the method devised by Reich, as modified by M'Cay,[2] 0·5 g. pyrites is treated with strong nitric acid in a porcelain crucible, the free acid evaporated without taking the mixture to dryness, 4 g. of sodium carbonate added, and the whole taken to dryness on the sand-bath, after which 4 g. of potassium nitrate is added, and the mixture heated to gentle fusion for ten minutes. The melt is extracted with hot water, filtered, and the filtrate, after acidifying with a little nitric acid, heated for some time to remove all carbon dioxide, and after addition of silver nitrate, cautiously neutralised with dilute ammonia. The precipitate, which contains all the arsenic as silver arsenate, is dissolved in dilute nitric acid, and either the silver estimated by titration with ammonium thiocyanate according to Volhard's method, or the solution evaporated in a platinum dish and the residue weighed. One part $Ag_3AsO_4 = 0{\cdot}1621$ As.

Other methods give results which differ rather widely from those obtained as above. Blattner and Brasseur[3] quote an instance in which different analysts found from 0·19 to 0·57 per cent. of arsenic, and another in which the figures varied from 0·05 to 0·39 per cent. Records of still greater differences may be found in the journals. The two authors quoted recommend the following process:—

1. *Wet treatment.* Ten g. of pyrites is added gradually with gentle warming to aqua regia, prepared from 125 c.c. nitric acid of sp. gr. 1·37, 250 c.c. hydrochloric acid of sp. gr. 1·15 to 1·17, and 100 c.c. water, in a litre flask. The bulk of the nitric acid is driven off by evaporation after addition of hydrochloric acid; since all the arsenic is present as arsenic acid, there is said to be no loss through evolution of arsenious chloride. After the addition of 100 c.c. of water, the solution is

[1] *Chem. Ind.*, 1905, **28**, 2; *J. Soc. Chem. Ind.*, 1905, **24**, 106; and *Chem. Zeit.*, 1910, **34**, 405; *J. Soc. Chem. Ind.*, 1910, **29**, 594.

[2] *Chem. News*, 1883, **48**, 7. *Amer. Chem. J.*, 1886, **8**, 77; 1887, **9**, 174; 1888, **10**, 459.

[3] *Bull. Soc. Chim.*, 1897 [3], **17**, 13.

cooled and filtered, ammonia is added until a slight precipitate of ferric hydroxide is formed, sulphurous anhydride passed through the cold solution until the reduction of the iron to the ferrous state is complete, the excess of sulphur dioxide removed by warming, and after cooling, to 60°-70°, the arsenic precipitated by passing in sulphuretted hydrogen for six to seven hours. The solution is allowed to stand for twelve hours, and then filtered. The precipitate is washed with water containing hydrochloric acid and sulphuretted hydrogen until all the iron has been removed, and finally with distilled water.

It is then dissolved by digesting the precipitate and filter paper with ammonium carbonate, and the solution filtered. The filtrate is rendered strongly acid with hydrochloric acid warmed to 50°-70°, and the arsenic precipitated as arsenious sulphide by passing in sulphuretted hydrogen for an hour. The arsenic in the precipitate may be determined either as magnesium ammonium arsenate or as silver arsenate. In the former case the precipitate is dissolved in strong ammonia, evaporated to dryness on the water-bath, taken up with 10 c.c. nitric acid, and after a further slight evaporation, rendered ammoniacal, and a small quantity of alcohol added, followed by magnesia mixture; after standing for twelve hours, the precipitate is collected on an ash-free filter paper, washed with a solution of one part of ammonium chloride and one of alcohol in three of water, dried, and ignited after separation from the filter paper. The filter paper is ignited separately after addition of a small quantity of ammonium nitrate. One hundred parts $Mg_2As_2O_7$ correspond to 48·28 parts As.

2. *Dry treatment.* Two g. of pyrites is thoroughly mixed in a platinum crucible of 30 c.c. capacity with 10 to 12 g. of a mixture of equal parts of potassium nitrate and sodium carbonate, and covered with a layer of 2 g. of the same mixture. The crucible is then covered and heated over a Bunsen flame 3 cm. high. When the reaction is complete, the mass is allowed to cool, the contents of the crucible placed in 70 c.c. of boiling water, and after solution, the whole filtered and the residue washed with boiling water. All the arsenic is then in the filtrate as arsenate. The solution is acidified with nitric acid, heated to boiling, allowed to cool, rendered exactly neutral by ammonia, and after the addition of one drop of nitric acid, again neutralised until a drop of the solution only produces a blue tint on red litmus paper after some seconds. Silver nitrate is then added, drop by drop, until no further precipitation occurs; the silver arsenate is collected on a filter and washed with cold water until the filtrate no longer gives a turbidity with hydrochloric acid. The silver arsenate is dissolved on the filter in very dilute nitric acid, 5 c.c. of a sulphuric acid—nitric acid—iron solution added as indicator, and the solution titrated with $N/10$ ammonium thiocyanate solution to the appearance of a rose

coloration. Each 1 c.c. of the thiocyanate solution corresponds to 0·0025 g. As. This method is rapid, and the results obtained agree very closely with those obtained by the first method, and also with those of Clark, who employs a mixture of magnesia and sodium hydroxide for fusing the ore (cf. *infra*).

This second method of Blattner and Brasseur is to be preferred to the first, in which a loss of arsenic by volatilisation as arsenious chloride may occur.

The same authors have also described a method[1] based on the precipitation of the arsenic as tri-iodide and the subsequent volumetric estimation of the latter.

List[2] heats 2 g. pyrites with 10 g. sodium peroxide in a crucible, as described on p. 371. By this treatment all the arsenic is converted to arsenic acid, which may be estimated as in the method of Blattner and Brasseur.

Clark[3] has devised the two following methods for the estimation of arsenic in pyrites:—

1. *Precipitation method.* About 3 g. of the ground sample is mixed with four times its weight of a mixture of equal parts of freshly calcined magnesia and pure sodium hydroxide previously ground together in a porcelain mortar, and the whole heated for about ten minutes in an uncovered platinum crucible; the mixture contracts slightly, but does not fuse. The product is extracted with hot water, and the filtrate acidified with hydrochloric acid, whereby sulphuretted hydrogen is freely evolved. On boiling the nearly colourless solution thus obtained for a few minutes, the arsenic separates as sulphide. After saturation with sulphuretted hydrogen to ensure complete precipitation, the precipitate is filtered off, washed, the arsenic trisulphide dissolved in ammonia, and the resulting solution evaporated to dryness on the water-bath. The residue is dissolved in a small quantity of strong nitric acid and the arsenic estimated as magnesium ammonium arsenate, or precipitated as silver arsenate, and its weight calculated from the silver found, as determined by titration by Volhard's method, or by cupellation according to Richter.

The method gives very accurate results, and is applicable even when the arsenic is only present in very small quantity.

2. *Distillation method.* About 1·7 g. of the finely powdered pyrites mixed with six times its weight of the magnesia and sodium hydroxide mixture is heated over a Bunsen flame of medium height in an uncovered platinum crucible for one hour, by which time oxidation should be complete. The contents of the crucible are transferred to a flask, moistened with water, and dissolved in about 70 c.c. of

[1] *Z. angew. Chem.*, 1904, **17**, 1727. [2] *Ibid.*, 1903, **16**, 415.
[3] *J. Soc. Chem. Ind.*, 1887, **6**, 352.

strong hydrochloric acid. It is necessary to heat towards the end, until all action ceases. The flask is fitted with a funnel tube which dips below the surface of the liquid, and it is further connected with a small glass cooling-worm, to the end of which a straight calcium chloride tube is attached. A considerable excess of reducing agent, dissolved in strong hydrochloric acid, is then admitted through the funnel tube. The reducing agent employed is cuprous chloride, which forms a readily soluble double salt with sodium chloride, and reduces quite as readily as a ferrous salt. A mixture of cuprous and ferrous chlorides, obtained by dissolving copper in ferric chloride, also forms an excellent reducing agent. The contents of the flask are then slowly distilled into water for an hour, after which about 30 g. of strong hydrochloric acid is added and the distillation continued for a further half-hour. All the arsenic should now be in the receiver, but it is advisable to check this by adding more hydrochloric acid, changing the receiver, and testing the fresh distillate collected. The arsenic so recovered may be precipitated as sulphide and collected on a tared filter paper, or it may be titrated with iodine in the usual manner.

The distillation method requires less time than any other, and gives equally exact results even for small amounts of arsenic. It may also be employed with advantage in estimating the arsenic in metallic copper.

According to H. Fresenius,[1] the fusion method offers no advantages over that of direct distillation in the presence of ferrous chloride, where the solution has been treated hot with chlorine or with hydrochloric acid and potassium chlorate.

The methods for detecting and estimating traces of arsenic are described on pp. 433-448.

4. **Copper.**—The following process is employed at the Duisburg copper works, and was first described in the *Alkali Makers' Handbook*. Five g. of the pyrites, ground and dried at 100°, are gradually dissolved in 60 c.c. nitric acid of sp. gr. 1·2 in an inclined Erlenmeyer flask. As soon as the violence of the reaction is over, the flask is warmed and evaporation allowed to proceed until sulphuric acid vapours are given off. The dry residue is dissolved in 50 c.c. hydrochloric acid of sp. gr. 1·19, and after the addition of sodium hypophosphite (2 g. sodium hypophosphite, NaH_2PO_2, dissolved in 5 c.c. water) the solution is boiled for a time to remove arsenic and to reduce the ferric chloride. An excess of strong hydrochloric acid is then added, the solution diluted with about 300 c.c. of hot water, sulphuretted hydrogen passed in, and the precipitate filtered off and thoroughly washed. A hole is made in the filter by means of a glass rod, the precipitate washed back into the precipitating flask, and the metallic sulphides adhering to the filter paper as well as the main bulk of precipitate, brought into solution by

[1] *Z. anal. Chem.*, 1888, 27, 34; *cf.* also, Nahnsen, *Chem. Zeit.*, 1887, 11, 692.

treatment with nitric acid; the solution in the flask is then evaporated to dryness on the water-bath, and the residue again taken up with nitric acid and water, neutralised with ammonia and dilute sulphuric acid added in slight excess. When cold, the solution is filtered to remove lead sulphate and other insoluble matter, the flask and the filter being washed with water containing sulphuric acid, 3 to 8 c.c. of nitric acid of sp. gr. 1·4 added to the filtrate, and the copper deposited electrolytically. From the weight of copper found, 0·01 per cent. is deducted for the simultaneously deposited bismuth and antimony.

Nahnsen[1] estimates the copper in pyrites as follows. The pyrites is very finely ground, dried, and 12·5 g. of the dried material is covered with 10 c.c. of water and 1 c.c. of strong sulphuric acid in a thin-walled beaker about 17 cm. deep. The beaker is covered with a porcelain dish and nitric acid of sp. gr. 1·4 added in successive small portions until frothing ceases to occur. The solution is then boiled over a fairly large flame; after several minutes the porcelain dish, which is sufficiently washed by the acid which condenses underneath, is removed and the gradually thickening solution is allowed to boil vigorously with constant agitation, until the liquid almost adheres to the glass and yellow particles of salt begin to separate. The magma is then quickly brought into solution by the addition of warm water. With some practice the whole operation may be performed in from ten to fifteen minutes. The cold solution is transferred to a 250 c.c. flask, made up to the mark and filtered through a dry filter paper. Two hundred c.c. (= 10 g. pyrites) of the solution, which is now free from silica and lead, is treated for some hours with a good current of sulphuretted hydrogen, until the precipitate becomes flocculent and the solution appears clear. The solution is then washed by decantation through a filter, the precipitate in the beaker being pressed out by means of a glass rod during the washing. It is unnecessary to wash copper sulphide with sulphuretted hydrogen water when, as in this case, the sulphuretted hydrogen has been allowed to act until the precipitate settles well and leaves a clear supernatant liquid. The portion of the precipitate remaining on the filter is washed back into the main bulk with the least possible quantity of hot water, and concentrated sodium sulphide solution added in such quantity that no sulphur remains undissolved after the solution has been brought to, and maintained for several minutes at, boiling point. After diluting with water and allowing to settle in a warm place, the solution, which contains the arsenic and antimony, now quite free from copper, is filtered, and the sulphide of copper washed with hot water. Traces of iron sulphide, which always adhere to the sulphide of copper (in two cases this amounted to 0·02 per cent. on the pyrites), are extracted by washing with hot water

[1] *Chem. Zeit.*, 1887, 11, 692; *J. Soc. Chem. Ind.*, 1887, 6, 564.

acidified with a few drops of hydrochloric acid; the precipitate is then washed until free from chlorine, and the copper estimated as cuprous sulphide.

Cadmium and bismuth sulphides, present in the cuprous sulphide, are determined by dissolving the precipitate in nitric acid, and treating the warm solution for some time with ammonium carbonate. The resulting precipitate is weighed as oxide and allowed for.

Should 25 g. be taken for analysis instead of 12·5 g., the method, according to the author, is but slightly more troublesome and longer. When the pyrites contains 3 to 5 per cent. of copper, 5 g. of the sample will suffice.

A very complete account of the estimation of copper in pyrites, and more particularly of the "Cornish assay," has been published by Westmoreland,[1] and more recently methods have been described by Treadwell[2] and Demorest.[3]

List[4] burns the pyrites in a porcelain crucible of special shape, extracts with hydrochloric acid, neutralises with ammonia, adds sulphurous acid, and precipitates the copper as cuprous thiocyanate; this is oxidised with a mixture of sulphuric and nitric acids to sulphate, and the copper determined by electrolysis.

5. **Lead.**—Lead remains in the residue in the form of sulphate when the pyrites is treated with aqua regia, as described on p. 367. The lead sulphate is extracted from the insoluble residue by warming with a concentrated solution of ammonium acetate; the resulting solution is evaporated with addition of a little pure sulphuric acid, and the residue finally dried and ignited in a porcelain dish or crucible. One part $PbSO_4$ = 0·6831 Pb.

6. **Zinc.**—The zinc in pyrites is occasionally determined, according to Hassreidter and Prost, since it is scarcely possible to recover the sulphur combined with the zinc. Schaffner's method, as described under Zinc Blende on p. 383, is not available, owing to the large preponderance of iron, and on this latter account a gravimetric method must be employed. One g. of the pyrites is dissolved in aqua regia, as described on p. 367, the excess of nitric acid evaporated off, and the residue taken up with 5 c.c. of strong hydrochloric acid; water is then added and the solution treated with sulphuretted hydrogen to remove any metals yielding sulphides insoluble in acid solution. Any precipitate formed is filtered off, the filtrate freed from sulphuretted hydrogen by boiling and oxidised with aqua regia. The oxidised solution is treated, when cold, with ammonium carbonate, until the resulting precipitate only redissolves very slowly; ammonium acetate is then added, the solution boiled for a short time, and filtered. The basic

[1] *J. Soc. Chem. Ind.*, 1886, 5, 49 and 277.
[2] *Chem. Zeit.*, 1912, 36, 961.
[3] *J. Ind. Eng. Chem.*, 1913, 5, 215.
[4] *Z. angew. Chem.*, 1903, 16, 416.

ferric acetate so precipitated carries down some of the zinc, and must, therefore, be dissolved in hydrochloric acid, and again precipitated as described, the operation being repeated so long as zinc can be detected in the filtrate. The combined filtrates are concentrated if necessary, and the zinc precipitated in the warm solution by sulphuretted hydrogen; the whole is then allowed to stand for twenty-four hours, the clear liquor decanted, and the zinc sulphide filtered off and washed. The precipitate and filter are treated with dilute hydrochloric acid, and the resulting solution, after boiling till free from sulphuretted hydrogen, filtered, precipitated with sodium carbonate, the zinc carbonate well washed, dried, and converted by ignition to ZnO of which one part = 0·8033 Zn. For very exact determinations any silica, oxide of iron, and alumina precipitated with the zinc oxide must be estimated and allowed for; this, however, is seldom necessary.

Mayer and Lösekann[1] have worked out a method for estimating the zinc as zinc ammonium phosphate.

7. **Carbonates of the alkaline earths** are occasionally determined, since when present they cause sulphur to be retained, owing to the formation of the corresponding sulphates. Since their quantity is always small, the carbonic acid cannot be determined accurately by loss, and consequently a direct method must be used. The carbonic acid is liberated by addition of strong acid and absorbed in soda lime, taking care to retain moisture and any acid carried forward; either the apparatus of Fresenius[2] or that of Classen[3] may be employed for the determination. Greater rapidity and accuracy can be attained by measuring the volume of evolved gas in the Lunge and Marchlewski calcimeter[4] (see p. 615).

8. **Carbon**.—It is occasionally necessary to estimate the carbon present in pyrites, especially in the products sorted out from coal and known under the name of "coal brasses."[5] This is done, according to Treadwell and Koch,[6] by combustion in a porcelain boat, as in the ordinary method of organic analysis, employing a 30 cm. layer of copper oxide and 25 cm. of lead peroxide to retain the sulphur; or more conveniently and in shorter time by oxidising with a mixture of chromic and sulphuric acids. For the latter process they follow the method of Corleis,[7] passing the gas liberated in the decomposing flask through a 10 cm. layer of glowing copper oxide, followed by 10 cm. of solid chromium trioxide, and after this through two small U-tubes each containing 3 c.c. of a solution of chromium trioxide in concentrated

[1] *Chem. Zeit.*, 1886, **10**, 729.
[2] *Quantitative Analysis*, 6th edition, vol. i., p. 341.
[3] *Cf.* Treadwell, *Analytical Chemistry*, 5th edition, vol. ii., p. 380.
[4] *Z. angew. Chem.*, 1891, **4**, 229.
[5] *Cf.* W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, 1923, p. 122.
[6] *Z. angew. Chem.*, 1903, **16**, 173.
[7] *Stahl u. Eisen*, 1894, **14**, 587; *cf.* Vol. II., "Iron."

sulphuric acid. After leaving the U-tubes the gas is passed through a tube filled with glass beads moistened with sulphuric acid, then through two of calcium chloride tubes, and is finally absorbed in two weighed tubes filled with soda-lime. The results obtained in this manner were identical with those of the combustion method (26·26 per cent. carbon).

9. It is necessary in some instances to distinguish between **Ordinary and magnetic pyrites (Pyrrhotite)**, Fe_7S_8, more especially in the case of American ores. To effect this,[1] the mineral is ground till it will pass through a sieve of sixty meshes to the inch (24 per cm.), but not finer, and the powder spread on a sheet of glazed paper. The magnetic pyrites is then picked out by the aid of a magnet and freed from any ordinary pyrites adhering mechanically, by gently tapping the magnet, after which the armature is fixed to the magnet and the magnetic ore brushed off. This operation is repeated five or six times and the sulphur separately estimated in the two portions.

A scheme for the complete analysis of pyrites has been published by Vilstrup.[2]

IV. Zinc Blende

1. **Total Sulphur**.—0·5 g. of the very finely ground sample is covered with about 20 c.c. of a mixture of three parts strong nitric acid and one part strong hydrochloric acid, or with hydrochloric acid saturated with bromine, allowed to stand covered overnight, evaporated almost to dryness, and a few c.c. of hydrochloric acid and 50 c.c. of water added; the solution is filtered hot and precipitated with barium chloride, after removal of the iron by ammonia, as described on p. 367, should the iron be present in any quantity.

According to Thiel,[3] the determination of sulphuric acid in the presence of large quantities of zinc always leads to low results, owing to the formation of complex salts on precipitation with barium chloride (with equivalent quantities of zinc the results are 0·33 per cent. too low). This source of error may be avoided if, before the addition of the barium chloride, the zinc is exactly precipitated as hydroxide by addition of ammonia, and the hydroxide subsequently dissolved out of the mixed precipitate with a slight excess of hydrochloric acid before filtering.

2. **Zinc.**—According to the modified Schaffner method now employed at zinc works,[4] 2·5 g. of the blende, dried at 100° and finely ground, is treated with 12 c.c. of fuming nitric acid in an Erlenmeyer flask of 200 c.c. capacity, first in the cold and then with gentle heating to disappearance of the red fumes, when 20 to 25 c.c. of strong nitric acid is added

[1] Cone, *J. Amer. Chem. Soc.*, 1896, **18**, 404.
[2] *Chem. Zeit.*, 1910, **34**, 350; *J. Soc. Chem. Ind.*, 1910, **29**, 560.
[3] *Z. anorg. Chem.*, 1903, **36**, 85.
[4] Communicated by V. Hassreidter and E. Prost.

and the whole evaporated to dryness on the sand-bath. Five c.c. of hydrochloric acid and a little water are then added and the mixture warmed until as much as possible has dissolved, after which the solution is diluted with 50 to 60 c.c. of water and the whole heated to 60° to 70°, until only gangue and separated sulphur remain undissolved. A moderate current of sulphuretted hydrogen is next passed into the solution and 50 to 100 c.c. of cold water added, little by little, with continuous stirring until the precipitation of lead and cadmium sulphides is complete, which may be recognised by the transparency of the bubbles as they rise through the solution. Excessive dilution and too slow a current of sulphuretted hydrogen should be avoided. The solution is filtered and the precipitate washed with 100 c.c. of sulphuretted hydrogen water, to which 5 c.c. of hydrochloric acid has been added, until a drop of the filtrate ceases to give the reaction for zinc with ammonium sulphide. The filtrate and washings, which amount in all to about 300 c.c., are boiled to remove the sulphuretted hydrogen, the complete removal of which is ascertained by lead acetate paper, and the ferrous iron then oxidised by addition of 5 c.c. of strong nitric acid and 10 c.c. of hydrochloric acid. After partial cooling the solution is poured into a 500 c.c. flask, 100 c.c. of ammonia of sp. gr. 0·9 to 0·91 and 10 c.c. of a cold saturated solution of commercial ammonium carbonate added, and the whole well shaken and allowed to cool.

In the meantime an ammoniacal solution of known zinc content is prepared, by dissolving in a 500 c.c. flask chemically pure zinc, approximately equal in quantity to the zinc content of the ore, in 5 c.c. of nitric acid and 20 c.c. of hydrochloric acid diluted with about 250 c.c. of water. After solution, 100 c.c. of ammonia and 10 c.c. of a saturated solution of ammonium carbonate are added, the whole shaken, and allowed to cool. In the presence of manganese, 10 c.c. of hydrogen peroxide is added before the ammonia. When quite cold, both flasks are filled with water to the graduation mark, and the solution prepared from the ore passed through a dry, pleated filter paper. For titration, 100 c.c. is pipetted from each solution into a thick-walled glass cylinder or beaker, and each portion diluted with about 200 c.c. of water. The standard solution for titration consists of a concentrated solution of commercial sodium sulphide crystals diluted with 10 to 20 times its volume of water, so that each c.c. corresponds to 0·005 to 0·010 g. of zinc. The sodium sulphide solution is allowed to flow alternately from two adjacent 50 c.c. burettes into each of the two solutions, at first in 2 or 3 c.c. at a time, and later in such smaller quantities as may appear necessary; the solutions are stirred and a drop of each solution placed simultaneously, by means of thin glass rods, on a strip of sensitive lead acetate paper. After ten to fifteen seconds have elapsed, the drops are washed off by the aid of a small wash-bottle, and the titration with

the sulphide solution continued until the drops taken from each of the solutions, after an equal lapse of time, give rise to weak but distinctly perceptible brown stains of equal intensity. Should the volume of liquid withdrawn for the tests be appreciable, the operation must be repeated; in all cases the end-reactions in the two solutions must be reached at the same time and the readings made to within 0·05 c.c.

If the quantity of pure zinc taken for the standard solution be denoted by a, the number of c.c. of the sodium sulphide solution required per 100 c.c. of the standard by b, and the number of c.c. required per 100 c.c. of the solution of the ore (=0·5 g. ore) by c, then the percentage of zinc in the ore is given by the formula $\frac{40\,ac}{b}$.

In very exact determinations a quantity of ferric chloride, corresponding to the iron content of the ore, should be added to the standard solution, to compensate for the zinc carried down with the ferric hydroxide precipitate.

The zinc may also, and perhaps preferably, be determined by the ferrocyanide method (see "Zinc," Vol. II.). The solution, freed from other metals, and having the iron precipitated, as for Schaffner's method, is filtered into a 500 c.c. flask; the ferric hydroxide is dissolved in acid, reprecipitated, and the solution filtered into the same flask. After washing the precipitate free from zinc, the solution is made up to the mark and an aliquot portion neutralised with hydrochloric acid, an excess of 5 c.c. of acid added, the bulk made up to about 250 c.c. with hot water, and titrated with a solution of potassium ferrocyanide solution, till a drop spotted on a 5 per cent. uranium acetate solution shows the beginning of a brown colour. The ferrocyanide solution contains about 45 g. of the crystallised salt per litre, so that 1 c.c. is approximately equivalent to 0·01 g. of zinc, but its value must be fixed by titration of a solution of a known amount of pure zinc in hydrochloric acid.

F. Meyer[1] treats 0·5 g. of the ore, in an ordinary flask, with 10 c.c. of aqua regia (made up of two parts of hydrochloric to one part of nitric acid), starting cold and then warming, evaporates off the excess of acid, takes up the residue with 10 c.c. of sulphuric acid (1 : 2), and evaporates the solution, to precipitate the lead, until dense white fumes are evolved. He then allows the solution to cool, dilutes with 60 to 80 c.c. of hot water, precipitates copper, cadmium, etc., by the addition of 10 c.c. of sodium thiosulphate solution (1 : 8), boils until the solution is nearly clear, and, after filtering from gangue, lead sulphate, etc., and boiling the filtrate with 5 c.c. of nitric acid until the sulphur has collected into globules, precipitates the iron and aluminium with 30 c.c. of ammonia of sp. gr. 0·92; finally, when nearly cold, the manganese is thrown

[1] *Z. angew. Chem.*, 1894, 7, 391.

down by the addition of 20 c.c. of bromine water. After standing for some time the bromine is expelled by boiling, the solution filtered into a thick-walled beaker, the flask and filter paper partially washed, the contents of the filter dissolved in 5 c.c. of aqua regia and collected in the flask, the iron, aluminium, and manganese precipitated as before by 20 c.c. of ammonia solution and 20 c.c. of bromine water, the filtrate added to the preceding and the two made up to 500 c.c. The solution is then allowed to stand overnight and titrated with sodium sulphide or potassium ferrocyanide, as described above.

Jensch[1] has drawn attention to the occurrence of certain siliceous zinc ores which obstinately resist the ordinary methods of treatment.

When the zinc is determined gravimetrically, it is necessary, as a rule, to separate the zinc from the other metals. The ordinary method consists in precipitating as sulphide with sulphuretted hydrogen in acetic acid solution, or by adding ammonium sulphide. In either case great difficulty is experienced in the filtration of the sulphide, which readily passes through the filter paper. This difficulty may be quite overcome if Murmann's suggestion[2] of adding a solution of mercuric chloride before precipitation be followed; the mixed precipitate of the sulphides of zinc and mercury settles in a few minutes, and yields a clear solution on filtration. On ignition, the mercuric sulphide is completely eliminated, whilst the sulphide of zinc is converted into the oxide, even in the absence of a current of oxygen. Herting strongly recommends this mode of procedure. He also confirms the observation of Flath,[3] to the effect that zinc may be completely separated from iron by a double precipitation of the latter with ammonia, especially after the addition of ammonium acetate.

On the determination of zinc in blendes, see also Herz,[4] Brunck,[5] Herting,[6] and a critical discussion in *Metall u. Erz*, 1920, **17** (viii.), 452.

3. **Lead.**—The metallic sulphides precipitated as above (2) are, if necessary, digested with a moderately concentrated sodium sulphide solution, the resulting solution diluted, filtered, and the insoluble matter washed. The residue is dissolved in dilute nitric acid, the solution filtered and evaporated with excess of sulphuric acid, to obtain the lead in the form of sulphate. One part $PbSO_4 = 0{\cdot}6832$ Pb.

4. **Calcium and Magnesium** fix sulphur during calcination, and must consequently be estimated. Two to 5 g. of the blende is digested by warming with 50 c.c. of dilute hydrochloric acid (1 : 10), the solution decanted, and the operation repeated once or twice. The residue is washed, the filtrate freed from sulphuretted hydrogen by boiling, oxidised by bromine water, and precipitated with ammonia free from

[1] *Z. angew. Chem.*, 1894, **7**, 155.
[2] *Monatsh.*, 1898, **19**, 404.
[3] *Chem. Zeit.*, 1902, **26**, 611.
[4] *Z. anorg. Chem.*, 1901, **26**, 90.
[5] *Chem. Zeit.*, 1903, **27**, 339.
[6] *Ibid.*, 987.

carbonate. The calcium in the filtrate is precipitated in the usual way by addition of ammonium oxalate, and, after strong ignition, weighed as oxide; the magnesium is determined by the addition of ammonium phosphate to the filtrate from the oxalate. (Cf. *infra* under Sulphate.)

5. **Arsenic,** as described above, p. 376.

6. **Carbonic Acid** may be estimated as described under Pyrites (p. 382). This estimation is of some importance, since blende occasionally contains spathic iron ore and calamine, in addition to calcium and magnesium carbonate.

7. **Fluorine** is determined, according to Prost and Balthaser,[1] by mixing 5 g. of the blende with powdered quartz, heating with sulphuric acid, condensing the liberated silicon fluoride in water, filtering off the separated silica, precipitating the hydrofluosilicic acid with potassium chloride and alcohol, and weighing on a tared filter paper. This method gives results from 0·6 to 0·8 per cent. too low.

Bein[2] estimates the fluorine indirectly, from the silica separated as above. This method is, however, inexact.

Bullnheimer[3] obtained the best results by the following modification of the method of Fresenius.[4] An Erlenmeyer flask of 300 to 350 c.c. capacity is fitted with a rubber stopper, bored in three places, for a thermometer and for inlet- and outlet-tubes respectively. To the last is connected a U-tube filled with glass wool, and beyond this a Winkler cooling worm, which is cooled by immersion in water; a Drehschmidt wash-bottle filled with 80 c.c. of potassium chloride solution is attached to the worm. The inlet-tube is intended, as in the Fresenius method, for admission of air, previously dried and purified by sulphuric acid and soda-lime. About 2·5 g. of the blende is intimately mixed with from 3 to 5 g. of powdered quartz, and treated in the flask with 20 g. of chromic acid and 100 c.c. of concentrated sulphuric acid. Should the chromic acid be not absolutely dry, it must be mixed with the sulphuric acid before adding it to the ore. The flask is quickly stoppered, shaken, and a current of air passed through, at first in the cold, and subsequently with gradual heating to about 80°. When the evolution of oxygen begins to slacken, further heat is applied, until the temperature reaches 150° to 160°; so long as oxygen is coming off, the current of air may be discontinued. The reaction proceeds sometimes quietly, at other times violently. After three hours' heating, all the silicon fluoride should have been driven over into the receiver, and nothing more should be evolved from the absorption flask. The contents of this flask are then emptied out, an equal volume of alcohol

[1] *Z. angew. Chem.*, 1901, **14**, 101.
[2] *Z. anal. Chem.*, 1887, **26**, 733.
[3] *Z. angew. Chem.*, 1901, **14**, 103.
[4] *Quantitative Analysis*, 6th edition (1876), vol. i., p. 328.

added, the mixture allowed to stand for a time, and then titrated with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. The titration must be done rapidly, and the reading taken at the first reddening of the indicator.

8. Available Sulphur. — From the total sulphur, estimated as directed on p. 383, there must be deducted :—

for	1	part	Pb found	in No.	3	0·1595	parts S,
„	1	„	CaO	„	4	0·5712	„ S,
„	1	„	MgO	„	4	0·7943	„ S.

The quantity of sulphur remaining after these deductions is that available for the production of sulphuric acid. Any sulphur present as heavy spar remains in the insoluble residue from the original extraction.

CONTROL OF WORKING CONDITIONS

The objects to be aimed at in the production of sulphurous acid are (i) the fullest possible utilisation of the raw material employed, and (ii) the correct admixture of air. The former is controlled by the analysis and the appearance of the cinders, and the latter by examination of the products of combustion. Anemometers find but little application at this stage, but may be of great importance during the subsequent conversion of sulphurous acid to sulphuric acid.

I. Burnt Ore.—(Residues after Calcination.)

Crude or native Sulphur.—An analysis is scarcely necessary, since with the small quantity of fixed residue usually present, it is apparent to the eye whether combustion has been complete or not. Should it be deemed desirable, the residue is examined by ignition in a porcelain dish, or by oxidation with aqua regia.

Gas Residuals.—The residues in this case contain iron oxide and frequently lime also. The presence of the latter renders a determination of the total sulphur of little value; the available sulphur must be estimated by the method given on p. 364.

Iron Pyrites.—The sulphur in pyrites cinders may exist either as sulphide or as sulphate. In pyrites containing lead or zinc, it is impossible to decompose completely the sulphates of these metals in the kiln, whilst with cupriferous pyrites the complete burning-off of the sulphur is not desirable in view of the subsequent working up of the burnt ore for copper by the "chlorinating roast," and the burnt ore may contain, according to circumstances, from 3 to 5 per cent. of sulphur; in burnt ore from mixed pyrites there may be even larger quantities. On the other hand, with pure iron pyrites, the sulphur may be reduced to 1 per cent., at all events in the case of "smalls."

As a rule, only the total sulphur is determined in the burnt ore; in the case of cupreous pyrites the copper, and less frequently the iron, is also determined.

Sulphur. The wet method (p. 366) is seldom employed for this determination, partly because it is more troublesome than in the case of the ore, and also because rapid dry methods which are available are sufficiently accurate (*cf.* p. 371). If the cinders are intended for use in blast furnaces, Jene[1] states that the dry methods of determination should always be used, as the wet methods do not give the total sulphur; this has been confirmed by Gottlieb.[2] Many of these dry methods are, however, untrustworthy or not sufficiently convenient.

The method proposed by Böckmann is as follows:—A sample of the burnt ore from the kilns is taken every twelve hours, each kiln being provided with two sample boxes, one large and one small, numbered to correspond to the kiln. The samples are in the first instance collected in the smaller receivers and brought in these to the laboratory, where they are transferred to the corresponding larger boxes. At the end of the week's working a good average sample is drawn from the latter, broken down in an iron mortar, the coarsely ground sample so obtained divided by quartering on a piece of stout paper, and one of the quarters finely ground and sieved. The ground samples are filled into bottles, also numbered to correspond to the kilns. Finally, several grams of each sample are ground in successive small portions in an agate mortar until no grittiness is felt on rubbing between the fingers.

For the sulphur determination 1·5 to 2 g. of the very finely ground material is weighed off, and mixed with about 25 g. of a mixture of six parts sodium carbonate and one part potassium chlorate; this mixing is done in a large platinum dish, by the aid of an agate pestle fixed to a wooden handle. The mixture is then fused over the blowpipe. The melt is allowed to cool till only just warm, then covered with hot water, heated to boiling, and both the solution and the insoluble residue washed into a 250 c.c. flask. The contents are cooled, made up to the 250 c.c. mark, and $\frac{4}{5}$ of the solution filtered through a pleated filter paper into a 200 c.c. flask. The insoluble portion of the melt (oxides of iron, copper, etc.) only occupies a small volume, and it is unnecessary to make any correction for this. The solution is acidified with hydrochloric acid and the sulphuric acid estimated in the usual manner. Böckmann also suggests the use of this method for the determination of sulphur in pyrites, taking in that case 0·5 g. of the sample.

The method devised by Watson[3] is much more rapid than that of

[1] *Chem. Zeit.*, 1905, **29**, 362. [2] *Ibid.*, 1905, **29**, 688.
[3] *J. Soc. Chem. Ind.*, 1888, **7**, 305.

Böckmann, but it is unsatisfactory in its original form, owing to the difficulty of preventing the very finely divided oxide of iron from passing through the filter and thereby interfering with the end-reaction of the titration. Lunge[1] has modified the process so as to overcome this difficulty, whereby the method has been rendered convenient and rapid, and accurate to within 0·2 per cent. The Watson-Lunge method is as follows:—

Exactly 2 g. of sodium bicarbonate of known alkalinity is intimately mixed by means of a flattened glass rod with 3·2 g. of the ground cinders in a nickel crucible of 20 to 30 c.c. capacity; the mixture is heated for ten minutes over a small gas flame the tip of which just touches the bottom of the crucible. The crucible must be covered during this preliminary heating, and the contents must not be disturbed during this period lest some of the material be carried away by the gas evolved. Finally the heating is continued for fifteen minutes over a larger flame; the mixture is stirred frequently during this period, and the temperature must not be allowed to rise sufficiently high to cause fusion.

To prevent absorption of sulphur from the combustion products of the gas, it is best to support the crucible in a hole cut in an obliquely placed asbestos card, as shown in Fig. 173, p. 332, or in a fused silica plate. The arrangement proposed by D. Pfeiffer[2] is perhaps preferable. By the action of atmospheric oxygen the sulphur is converted into sulphate at the cost of a corresponding quantity of the bicarbonate. The contents of the crucible are emptied into a porcelain dish, the crucible washed out with water and the solution boiled for ten minutes with the addition of a saturated solution of sodium chloride; without this addition it is difficult to prevent some oxide of iron passing through the filter paper at a later stage. The insoluble residue is then filtered off and washed until free from alkali, the filtrate cooled, and the unchanged sodium carbonate titrated with normal hydrochloric acid (of which 1 c.c. = 0·0530 g. Na_2CO_3, corresponding to 0·01603 g. S), using methyl orange as indicator. If 2 g. bicarbonate require a c.c. of normal acid and the final solution requires b c.c., then the percentage content of sulphur = $\frac{a-b}{2}$.

The method is not applicable to pyrites containing much zinc (*cf.* p. 393), nor to zinc-free cinders which contain 6 per cent. or more of sulphur. For the latter the following mixture must be substituted for that given above, in order to ensure complete oxidation and at the same time to guard against fusion:[3]—1·603 g. of the sample, 2·0 g. sodium bicarbonate, 4 g. potassium chlorate, and 2 to 3 g. ferric oxide, free from

[1] *Z. angew. Chem.*, 1892, **5**, 447.
[2] *Chem. Zeit.*, 1904, **28**, 38.
[3] Lunge, *Z. angew. Chem.*, 1906, **19**, 27.

sulphur. The determination is otherwise conducted as above; the sulphur percentage $= a - b$.

The sodium chloride employed must be quite pure, that is, not only react perfectly neutral, but also be free from calcium and magnesium chlorides, which, if present, would naturally fix a corresponding quantity of sodium bicarbonate.

Conner[1] heats 1 g. of the finely pounded sample, in a combustion boat, in a silica tube at 1000° and passes a current of air, free from carbon dioxide, through the tube. The whole of the sulphur is burnt out, and the oxides formed are absorbed in $N/10$ sodium hydroxide, the excess of which is determined after the combustion is over (about fifteen minutes) by titration with $N/10$ acid and phenolphthalein.

List and Moore[2] apply the sodium peroxide method (p. 371) to burnt ore.

The following process is employed in one of the largest French works for the regular daily control of the calcination; it enables a large number of sulphur tests in burnt ore to be carried out simultaneously, and the results are obtained in a comparatively short time. The method depends upon the fact that at a red heat hydrogen will decompose all sulphur compounds of iron with the formation of sulphuretted hydrogen. The sulphuretted hydrogen so liberated is passed into a standard solution of silver nitrate, and is estimated by titrating back the excess of this reagent according to Volhard's method (p. 74). The test is carried out as follows:—Several porcelain tubes, closed at both ends by non-vulcanised rubber stoppers carrying glass tubes, are arranged in a furnace heated by a six-flamed Bunsen burner. The glass tubes are connected at the inlet end with a hydrogen generator by means of a corresponding number of lengths of rubber tubing furnished with screw clips; the outlet pieces are connected with vertically bent tubes which dip into small test-glasses. The hydrogen used must be freed from any accompanying sulphuretted hydrogen by washing with silver nitrate solution. Each set is numbered, and the porcelain tubes, stoppers, inlet- and outlet-tubes and test-glasses are marked to correspond.

A preliminary test is first made to ensure that no precipitate results when the hydrogen is passed into the silver nitrate solution in the test-glasses. When this has been ascertained, exactly 1 g. of the finely ground cinders is weighed into a numbered porcelain boat, the boat pushed to the marked position in the porcelain tube by means of a glass rod, and 25 c.c. of silver nitrate solution (containing 10·604 g. $AgNO_3$, corresponding to 3·65 g. NaCl per litre) placed in each test-glass. When all the weighed samples are in position a current of hydrogen is passed through the tubes and regulated by means of the

[1] *J. Ind. Eng. Chem.*, 1913, 5, 399.
[2] *J. Ind. Eng. Chem.*, 1916, 8, 26.

screw clips to two to three bubbles per minute. After ten minutes when all the air has been expelled, the furnace is heated, at first gently, and then gradually raised to a red heat. After one and a half hours' heating, the elimination of the sulphur is complete. This is shown by no further cloudiness appearing in the silver nitrate solution, and by the improved and satisfactory settling out of the black precipitate of silver sulphide. The gas supply to the furnace is then gradually reduced, and the hydrogen current interrupted. The test-glasses are removed in turn, and without filtering off the precipitate, 1 c.c. of iron indicator (2·5 g. ferric nitrate dissolved in 100 c.c. nitric acid of sp. gr. 1·38) is added, and the solution immediately titrated with ammonium thiocyanate solution to permanent redness. The thiocyanate solution contains 4·752 g. per litre, and should correspond exactly with the silver nitrate solution. If the number of c.c. of ammonium thiocyanate required be denoted by a, then the percentage of sulphur in the pyrites cinders is given by the expression $\frac{25-a}{10}$.

Copper is estimated in the Duisburg works as described on p. 379, except that only 1 g. of the sample is employed, and solution effected by hydrochloric acid, to which a few drops of nitric acid have been added. Further, no deduction for bismuth and antimony is made from the weight of copper obtained by electro-deposition.[1]

List[2] ignites 5 g. of the cinders with 5 g. of sodium bicarbonate in an iron crucible, a treatment which renders the iron oxide readily soluble in strong hydrochloric acid. The copper in the solution thus obtained is estimated as described under pyrites (p. 379).

Iron. 0·5 g. of the burnt ore is taken, and the iron brought into solution by prolonged warming with strong hydrochloric acid; the boiling solution is then reduced by zinc free from iron, or, more conveniently, by stannous chloride, any excess of which is removed by the addition of a small quantity of mercuric chloride. The ferrous chloride solution so obtained is titrated with $N/10$ potassium dichromate solution, using ferricyanide as indicator, or is poured into 500 c.c. of water, to which has been added 20 c.c. of a solution containing, in a litre, 100 g. of manganous sulphate, 500 c.c. of 1 : 3 phosphoric acid, and 200 c.c. of concentrated sulphuric acid, and which has then been coloured pink by one or two drops of potassium permanganate solution. The iron content is arrived at by titration with $N/10$ potassium permanganate solution, of which each 1 c.c. equals 0·0056 g. Fe, or, on 0·5 g. of burnt ore, 1·12 per cent. of iron.

Zinc Blende.—Experiments by Lunge have shown that the Watson-

[1] *Cf.* Fresenius, *Z. anal. Chem.*, 1877, **16**, 338.
[2] *Z. angew. Chem.*, 1903, **16**, 416.

Lunge method (p. 389) for the determination of sulphur in burnt ore is not applicable to roasted blende; subsequent investigations by Lunge and Stierlin[1] have, however, proved that the oxidation can be satisfactorily effected by the addition of potassium chlorate to the sodium bicarbonate. 3·206 g. of the finely powdered and sieved sample is mixed with 2 g. of sodium bicarbonate and 2 g. of finely powdered potassium chlorate and heated for thirty minutes in a nickel crucible over a flame 3 to 4 cm. high, the tip of which is 2 to 3 cm. from the bottom of the crucible; after this interval the heating is continued for a further twenty minutes with a bigger flame, so that the bottom of the crucible is reached by the tip, and finally for ten minutes more with a still stronger flame, so that the bottom of the crucible is red hot, but without fusing the contents. The mass is then extracted and titrated as described under the Watson-Lunge method (p. 389). The method can also be applied to unburnt (green) zinc blende, if 2 g. of sulphur-free oxide of iron be added to the above mixture for the decomposition.

As an alternative the sulphur may be estimated gravimetrically, following the method described under raw blende (p. 383). The precipitation of the iron by ammonia may be omitted in the ordinary routine testing at works.

Nitchie[2] places 1 g. of the sample in a combustion boat, and heats it electrically in a silica tube to 1000° in a stream of air free from carbon dioxide, absorbing the sulphur oxides so produced in a measured volume of $N/10$ sodium hydroxide solution suitably diluted. When no more zinc fume is seen (usually after about six minutes' heating) the excess soda is titrated with $N/10$ acid and phenolphthalein. To the sulphur determined in this way must be added sulphur equivalent to the lime in the sample, if the total sulphur is required.

A rough guide to the progress of the calcination consists in treating the calcined ore in a flask with 10 c.c. of hydrochloric acid (1 : 2) and testing the evolved gas with neutral or slightly alkaline lead acetate paper; the extent of the calcination is judged by the degree of darkening obtained.[3] This test is employed by the foreman in the furnace room.

Zinc is estimated as on p. 383.

II. Examination of the Kiln Gases.

This examination extended formerly only to the determination of the percentage volume of sulphur dioxide in the gases, and was usually

[1] *Z. angew. Chem.*, 1906, **19**, 21.
[2] *J. Ind. Eng. Chem.*, 1912, **4**, 30; *J. Soc. Chem. Ind.*, 1912, **31**, 133.
[3] Meyer, *Z. angew. Chem.*, 1894, **7**, 7392.

carried out according to Reich's method,[1] the apparatus recommended by Lunge being as a rule employed (cf. *infra*). It has, however, been proved that the kiln gases always contain sulphuric anhydride, which may either be useful, as in the manufacture of sulphuric acid, or harmful, as in the preparation of sulphite liquor for use in the wood-pulp industry. The quantity of sulphur trioxide present may reach 10 per cent. of the sulphur content of the gas, and as it is not estimated in Reich's method of testing, the conclusions drawn as to the properties of the gas from the determination of the sulphur dioxide alone, may be quite erroneous, as has been shown by F. Fischer[2] from other considerations.

Lunge[3] consequently recommends the estimation of the total acidity in the gases, that is, SO_2+SO_3, by passing them through a solution of sodium hydroxide, coloured by phenolphthalein, until the colour disappears, instead of merely passing them through iodine solution. Other indicators are not suitable; phenolphthalein is the only one which indicates the simultaneous formation of sodium sulphite and sodium sulphate from the mixed gases. In the manufacture of sulphuric acid the Lunge test is generally sufficient for works purposes; Reich's test may, however, if desired, be employed in addition. Both tests should be carried out in the preparation of sulphite liquors, and also when the kiln gases are worked for sulphur trioxide and only the residual sulphur dioxide goes into the lead chambers.

Reich's method for the estimation of Sulphur Dioxide.—The kiln gases are drawn by means of an aspirator through water to which a measured quantity of iodine solution and some starch solution have been added. The end of the reaction is indicated by the disappearance of the blue colour. The volume per cent. of sulphur dioxide in the gases is calculated from the quantity of iodine solution employed and the volume of water aspirated, this latter being the equivalent of the non-absorbable portion of the gas.

Lowe[4] uses an iodide and iodate solution made by adding 127 g. of iodine to 30 g. of sodium hydroxide dissolved in water and diluting to 10 litres. A known quantity is used for the absorption, and after the passage of a measured volume of the gases the liquid is acidified and titrated with thiosulphate. The difference between the amount of thiosulphate used and that required by the same quantity of the original solution corresponds to the sulphur dioxide absorbed.

[1] F. Reich, "*Die bisherigen Versuche zur Beseitigung des schädlichen Einflusses des Hüttenrauches bei den fiskalischen Hüttenwerken zu Freiberg*, Freiberg, 1858." Special reprint from *Berg und Hütten Zeitung*; *cf.* also Winkler, *Industrie-Gase*, vol. ii., p. 350; and W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, 1923, p. 471.

[2] *Dingl. polyt. J.*, 1885, **258**, 28.

[3] *Z. angew. Chem.*, 1890, 3, 563.

[4] *J. Soc. Chem. Ind.*, 1921, **40**, 163T.

The arrangement of the Reich apparatus, as modified by Lunge, is shown in Fig. 189.

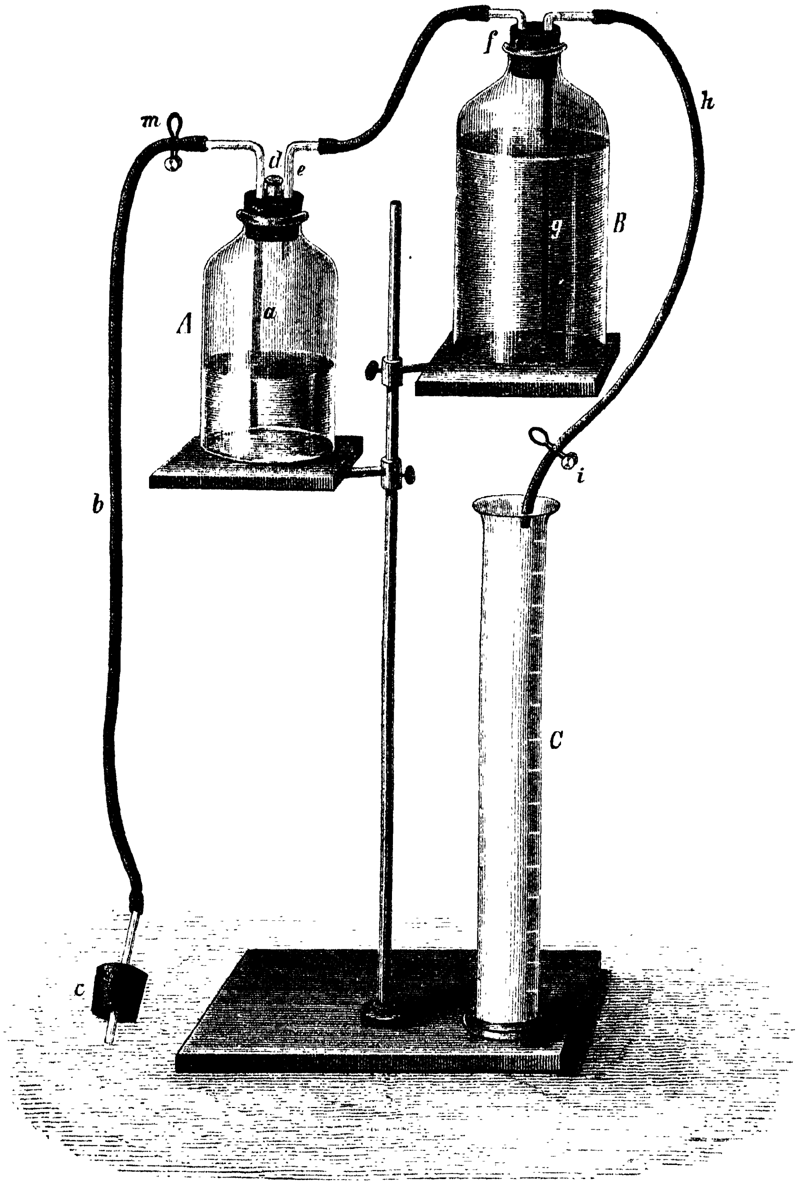

FIG. 189.

The bottle A has a capacity of about 200 c.c., B a capacity of 1000 c.c. After removal of the rubber stopper *d*, A is filled with distilled water to about a quarter of its capacity, and starch solution, sodium

bicarbonate, and sufficient iodine solution to produce a strong blue coloration added. The sodium bicarbonate increases the absorptive capacity of the iodine solution and at the same time overcomes any irregularity likely to occur in the course of the reaction. The bottle B is filled almost completely with water, and the cork *c* is then fitted in the hole especially made in the gas-main for the purposes of the test.

It is first necessary to test whether the apparatus is perfectly tight. With this object the spring clip *m* is closed and the clip *i* opened; the water should then only flow for a very short time. Should the water continue to flow the apparatus is not air-tight, and the leak must be located and repaired.

The rubber tubing *b* and the tube *a* are then filled with the kiln gas to be examined. To effect this the clip *m* is opened and then the clip *i* sufficiently to allow the water to flow slowly out and the gas to enter in single bubbles through *a* and rise to the surface of the liquid. As soon as decolorisation takes place the clip *i* is closed and 10 c.c. of $N/10$ iodine solution is added through the opening *d*.

Before starting a test, the gas to be examined must first be syphoned to the lower end of the tube *a*, so that the air contained in the vessel A may be at the same pressure as that obtaining in the subsequent operation. This is done by cautiously opening the clip *i* until the kiln gas is drawn to the desired point. The clip is then closed quickly, the water collected in C thrown away, and the measuring cylinder again placed in position. The clip *i* is then opened with the one hand and the flask A shaken with the other until the colour of the solution disappears, when the clip is closed and the volume of the water collected is read.

The reaction proceeds according to the equation :—

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

Consequently the 10 c.c. of iodine solution employed (=0·12692 g. I) corresponds to 0·03203 g. SO_2, or to 10·93 c.c. of SO_2 measured at 0° and 760 mm. Assuming that 128 c.c. of water has been collected in any one determination, this corresponds to 128 c.c. of non-absorbable gas drawn through the iodine solution. The total volume of gas aspirated is, therefore, 128+10·93 = 138·93 c.c., and the percentage volume of SO_2 :—

$$\frac{10.93 \times 100}{138.93} = 8 \text{ per cent.}$$

This calculation is avoided by making use of the following table :—

Cubic Centimetres Water collected.	Volume per cent. SO_2 in Kiln Gas.	Cubic Centimetres Water collected.	Volume per cent. SO_2 in Kiln Gas.
80·1	12	125·7	8
84·1	11·5	134·8	7·5
88·4	11	145·2	7
93·2	10·5	157·2	6·5
98·4	10	171·2	6
104·1	9·5	187·8	5·5
110·5	9	207·8	5
117·7	8·5	...	...

In this table no account is taken of variations in temperature and barometric pressure; should it be desired to correct for these, the volume read off is reduced to 0° and 760 mm. by Tables II. to IV. (Appendix), and the percentage volume of sulphur dioxide taken from the corrected volume by the above table. The necessary addition for the volume of the absorbed gas is included in the table.

Reich's method is not applicable to gases containing more than very small quantities of nitrogen acids. It cannot, for example, be employed in the case of gases leaving the chamber system, since the nitrogen acids contained in these would re-oxidise the hydriodic acid; but Raschig[1] points out that the addition of sodium acetate to the iodine causes the formation of sodium nitrite and acetic acid, and the iodine under these circumstances is decolorised solely by the sulphurous acid. (A subsequent titration of total free acid allows of the approximate determination of the nitrous acid.)

Reich's method gives the percentage of sulphur dioxide only during the short period of the test. Haller[2] has worked out a method which will give the average value over any period of time. He aspirates the gas (measuring, of course, the volume so aspirated) through a 10 per cent. solution of sodium hydroxide to which 5 per cent. of its volume of glycerin has been added. The addition of glycerin completely prevents the oxidation of the sulphurous acid. The sulphurous acid is then determined by neutralising the solution with hydrochloric acid, and then adding sufficient excess to ensure that the liquid at the end of the titration shall contain 15 per cent. of HCl, and titrating with potassium iodate solution.[3] A globule of chloroform is used as an indicator; this dissolves the iodine, first liberated, and is gradually decolorised as the addition of iodate converts this into iodine monochloride. The last portions of iodate must be added very gradually, with thorough shaking between, or there is a liability to overshoot

[1] *Z. angew. Chem.*, 1909, **22**, 1182; *J. Soc. Chem. Ind.*, 1909, **28**, 706.
[2] *J. Soc. Chem. Ind.*, 1919, **38**, 52T.
[3] Jamieson, *Amer. J. Sci.*, 1914, **38**, 166.

the end-point. The iodate solution is standardised against pure iodine; the equations are:—

$$4I + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O;$$

and

$$KIO_3 + 2H_2SO_3 + 2HCl = 2H_2SO_4 + KCl + ICl + H_2O.$$

Lunge's method for the estimation of Total Acids ($SO_2 + SO_3$).—The above apparatus may be employed, but the glass inlet-tube to the absorption flask should preferably be closed at the bottom, and the portion immersed in the solution pierced with a number of small holes to subdivide the stream of gas (Fig. 190). The gases are conducted through a solution of $N/10$ sodium hydroxide solution coloured with phenolphthalein until the colour is just discharged, the flask being continuously shaken during the absorption. The total acidity is usually calculated to sulphur dioxide by means of the table given above.[1]

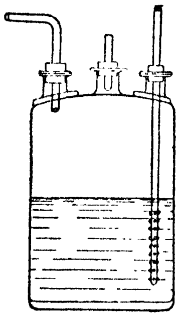

FIG. 190.

Berl[2] adds to the absorbing liquor 10 c.c. of a $\frac{1}{1000}$ molar solution of stannous chloride. This prevents oxidation of the sulphur dioxide, which can be titrated by iodine after the total acidity has been determined.

Errors may arise with both methods under certain conditions, owing to the presence of arsenious acid, which accumulates in the absorption tube; they are best guarded against by filtering the gases through asbestos.

Lunge employs the absorption bottle shown in Fig. 190, both for this test and for that of Reich. It has a capacity of 410 c.c., and is charged with 230 c.c. of water, 10 c.c. of $N/10$ sodium hydroxide solution, and 3 drops of phenolphthalein solution, for the total acidity determination. The gas is not aspirated continuously, as described above, but intermittently in such fashion that a volume of gas, much smaller than the free space in the bottle, is syphoned over, allowed to stand over the solution, shaken for about half a minute, then a further quantity of gas drawn over, and so on. A longer period of shaking is especially necessary towards the end of the absorption, and it is advisable to place a white ground below the flask to facilitate the observation of the colour change.

Richter[3] determines sulphur trioxide in furnace gases by condensation. A tube of refractory glass surrounded by an iron jacket is connected with a vertical absorption tube 30 to 40 cm. long, charged with pieces of broken porcelain surmounted by a layer of garnets, plugs of glass wool being packed above and below the charge. The tube is

[1] For further details, *cf.* Lunge, *Z. angew. Chem.*, 1890, **3**, 563.
[2] *Chem. Zeit.*, 1921, **45**, 693; *J. Soc. Chem. Ind.*, 1921, **40**, 580A.
[3] *Z. angew. Chem.*, 1913, **26**, 132; *J. Soc. Chem. Ind.*, 1913, **32**, 285.

surrounded by a freezing mixture, and the iron-jacketed tube being inserted in the flue of the furnace, a very slow current of the gases is drawn through the apparatus, and its quantity measured by means of an aspirator. The gas should be passed at the rate of about 1 litre in twenty-five minutes, and when a sufficient quantity has been treated, a current of pure air, dried by phosphorus pentoxide, since concentrated sulphuric acid yields small quantities of sulphur trioxide to the air, is drawn through to remove all traces of sulphur dioxide. The contents of the condensation tube are then washed out with water and the sulphuric acid is precipitated as barium sulphate. The condensation of the sulphur trioxide in a sufficiently long absorption tube is practically quantitative, and there is no necessity to use a second tube as a precaution.

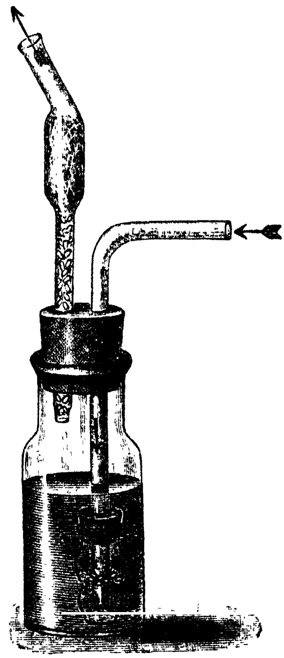

FIG. 191.

In the Thirty-fourth Report of the Inspector for Alkali Works (1897, p. 22), an absorption flask is described which gives good results even in the most difficult cases, such as, for example, the absorption of acid fog. It cannot be used for iodine solution, owing to the presence of rubber, but it is very suitable for the Lunge test, for the estimation of hydrochloric acid gas, and in many other cases. The apparatus is shown in Fig. 191 in half the actual size. The flask is fitted with a rubber stopper provided with an inlet- and exit-tube as shown. The former is 8 mm. wide, closed at the bottom, and pierced with a number of small holes, through which the gas passes to the double bulb, which is attached by means of a rubber stopper. The upper bulb is filled with small cuttings of rubber tubing, which are kept in motion by the stream of gas, which is thus brought into very intimate contact with the absorbing solution; the lower bulb is open at the bottom. The success of the apparatus depends largely on the correct dimensions being adhered to, thus: the lower opening of the double bulb is 6 mm. in diameter, the lower bulb 15 mm. and the upper 18 mm. in diameter, and the upper opening through which the inlet-tube passes 13 mm. wide. The gas passes from the bulb into the flask through several small holes, and finally leaves it through the exit-tube, which is narrowed below and widened above to form a cylindrical chamber; the lower, narrow portion is filled with the rubber rings and the upper, wider portion with glass wool. When used for the absorption

of acid vapours, the exit-tube is moistened with water coloured by methyl orange, which serves to indicate whether complete absorption is being effected in the bottle.

Lunge[1] has proposed to determine the acidity of kiln gases by measuring their specific gravity, a method which might be developed to give a continuous graphic record of the operation of the furnace. Differences of 1 per cent. of sulphur dioxide by volume affect the value of the specific gravity in the second decimal place, those of 0·1 per cent in the third decimal place. Such measurements might be made by a modification of the Lux gas balance, which, however, as at present constructed is not suitable for use with acid gases, or by the aid of F. C. Müller's[2] method of determining the density of gases. The "Ados" apparatus for the examination of flue gases might also be employed; this proposal, however, does not appear to have been worked out.

For the estimation of very minute amounts of sulphur dioxide in air, etc., see Sweeney, Outcault, and Withrow.[3]

III. Finished Products

These comprise, first, solutions of sulphurous anhydride in water, which, although seldom appearing on the market, are frequently obtained as intermediate products in many works, as, for example, in Hänisch and Schröder's process for the preparation of liquid sulphurous acid; secondly, liquid anhydrous sulphur dioxide; thirdly, the "sulphite liquor" of the wood-pulp industry, a solution of calcium or magnesium sulphite in aqueous sulphurous acid containing more or less sulphuric acid.

Solutions of Sulphurous Acid.—The determination of free sulphurous acid, or of that present as bisulphite, may be made acidimetrically by titration with normal alkali hydroxide solution, bearing in mind the behaviour of the indicator employed. Of the ordinary indicators, litmus is quite unsuitable, phenolphthalein gives the colour change to red when the normal salt, Na_2SO_3, has been formed, whilst with methyl orange the change to yellow corresponds to the formation of the acid sulphite $NaHSO_3$. In the absence of other acids (for example, sulphuric acid, which, if present, may be detected by barium chloride in hydrochloric acid solution), each 1 c.c. of normal alkali used will thus correspond to 0·03203 g. SO_2, when phenolphthalein is used as indicator, and to 0·06406 g. SO_2, when methyl orange is employed. Should free sulphuric acid or other strong mineral acid be present, the sulphurous acid may be determined along with the stronger acid, by titrating two

[1] *Z. angew. Chem.*, 1890, 3, 567. [2] *Ibid.*, 513.
[3] *J. Ind. Eng. Chem.*, 1917, 9, 949; *J. Soc. Chem. Ind.*, 1917, 36, 1233.

portions, the one with methyl orange, and the second with phenolphthalein as indicator. Less normal alkali will be used in the first than in the second case, in accordance with the behaviour of the two indicators towards sulphurous acid. The difference between the number of the c.c. used in the two cases, multiplied by 0·06406, gives the quantity of free sulphur dioxide in grams; the remaining alkali corresponds to the free strong mineral acid.

An alternative method of estimating free sulphurous acid in the presence of other free non-reducing acids, consists in running the acid into iodine solution, observing the precautions given on p. 67. One c.c. $N/10$ iodine solution corresponds to 0·003203 g. SO_2. Instead of iodine, hydrogen peroxide may be used, and the excess of peroxide determined by $N/10$ solution of potassium permanganate, by which the peroxide has originally been standardised.[1] Air-freed water must always be used for dilution in this method.

Pure aqueous solutions of sulphurous acid may also be tested by determining the specific gravity; further information on this point will be found in W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, p. 180. The following table, published by Giles and Shearer,[2] gives the specific gravities of solutions containing from 0·99 to 13·09 per cent. SO_2.

Specific gravity.	Temp. °C.	Per cent. SO_2.	Specific gravity.	Temp. °C.	Per cent. SO_2.
1·0051	15·5	0·99	1·0399	15·5	8·08
1·0102	15·5	2·05	1·0438	15·5	8·68
1·0148	15·5	2·87	1·0492	15·5	9·80
1·0204	15·5	4·04	1·0541	15·5	10·75
1·0252	15·5	4·99	1·0597	12·5	11·65
1·0297	15·5	5·89	1·0668	11	13·09
1·0353	15·5	7·01	...	...	...

Liquid sulphur dioxide may be examined in exactly the same way as solutions of sulphurous acid. The contained sulphuric acid may sometimes amount to as much as 20 per cent.[3]

Properties of liquid sulphurous anhydride :—

	At 0°.	At 15°.	At 30°.
Specific gravity . .	1·434	1·391	1·349
Vapour tension . .	1·5	2·7	4·5 Atmos.

One kg. corresponds to a gas volume of 342 litres at 0° and 760 mm.

[1] Craig, *J. Soc. Chem. Ind.*, 1919, **38**, 96 T. [2] *J. Soc. Chem. Ind.*, 1885, 4, 503.
[3] *Papier-Zeit.*, 1892, No. 62.

Critical temperature, 155°·4; critical pressure, 78·9 atm.; boiling point, at 760 mm. pressure, −11°; melting point, −76°.

Sulphites.—The normal sulphite and the acid sulphite present in sulphites (solid or in solution), may be estimated as follows. The total sulphurous acid is determined by titration with iodine, and the acid sulphite by titration of a second portion with standard alkali and phenolphthalein.

$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O.$$

One c.c. normal sodium hydroxide solution corresponds to 0·03203 g. SO_2 present as acid sulphite.

If the quantity of sulphurous acid present in a solution exceeds that necessary to form bisulphite, the solution is first titrated with normal sodium hydroxide and methyl orange until the red colour changes, phenolphthalein is then added, and the titration continued till the red coloration appears. Each 1 c.c. of the alkali required with methyl orange corresponds to 0·06406 g. SO_2 in the free condition, and each further c.c. required for the subsequent titration with phenolphthalein to 0·06406 g. SO_2 present as $NaHSO_3$, or half this quantity = 0·03203 g. as "half-free" sulphurous acid.

Jamieson's method (see *ante*, p. 397) may also be used for the determination of sulphurous acid in solutions of the acid or in sulphites.

Craig[1] determines sulphurous acid or sulphites by adding 0·5 to 1·0 g. to excess of hydrogen peroxide, acidifying with 10 c.c. of 1 : 3 sulphuric acid, cooling the solution, and titrating the excess of hydrogen peroxide by permanganate. The strength of the peroxide is, of course, determined in the first place by permanganate.

Sulphite Liquors for the manufacture of Wood-pulp.—The following estimations are necessary:—

1. *Total content of sulphurous acid.* The sulphite solution, which usually contains about 50 g. of sulphur dioxide per litre, is preferably diluted to twice its volume and the diluted solution allowed to flow from a burette into 25 c.c. of an acidified $N/10$ iodine solution until the colour is discharged (*cf.* p. 67). The volume of the iodine solution employed oxidises 0·080075 g. SO_2, consequently the volume of sulphite liquor used for the titration contains this total amount of free and fixed sulphur dioxide.

2. *Content of half-free and of free sulphurous acid*, that is, all sulphur dioxide over and above that required for the formation of calcium sulphite and which is present in the half-free condition as acid sulphite or as free sulphur dioxide in solution, in the liquor. The quantity present is arrived at by titration with normal sodium hydroxide solution, using phenolphthalein as indicator. Each 1 c.c. alkali used corresponds to 0·03203 g. SO_2 in the half-free or free state.

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 96T.

SULPHURIC ACID MANUFACTURE

RAW MATERIALS

These have already been described under—*Sulphur* (p. 358), *Spent oxide* (p. 364), *Pyrites* (p. 366), *Zinc blende* (p. 383). See also *Nitre* (p. 470) and *Nitric acid* (p. 489).

CONTROL OF WORKING CONDITIONS

In the manufacture of sulphuric acid by the lead-chamber process, many factors have to be taken into account, and a certain relationship must exist between these for the regular and satisfactory working of the plant. These factors comprise more especially the temperatures in the various parts of the system, the colour of the gases in the chambers, the draughts, the strengths of drip- and bottom-acid, of the Gay-Lussac and Glover acids (also the temperature of the last), the quantity of nitrogen oxides present in the acids, the composition of the gases, etc.

The rules to be observed in, and the conclusions to be drawn from, these observations are fully described in Lunge's *Sulphuric Acid and Alkali*.[1]

This section is restricted to a description of such methods of investigation as are essential to the satisfactory carrying out of the process.

EXAMINATION OF THE GASES

It is necessary to differentiate: *Inlet gases*, *Chamber gases* from various parts of the system, and *Exit gases* beyond the Gay-Lussac tower.

The examination of the inlet gases (kiln gases from the burning of pyrites or blende) has been described under the preparation of sulphurous acid (p. 393). The determination deals solely with the estimation of sulphur dioxide and sulphur trioxide. It is unnecessary to estimate the oxygen accompanying these gases, since it must always, in normal working, be in reciprocal relationship to the sulphur oxides present.

The examination of the gases in the chambers is generally carried out by observing the colour (more particularly in the hind portion of the system and at the exit), the temperature as measured by means of thermometers inserted at different places in the walls of the chambers, and the pressure, for which purpose the manometers and anemometers described on p. 167 *et seq.* may be employed, though frequently this is only done in a very crude manner by removing plugs or lutes.

[1] Fourth edition, p. 904 *et seq.*

Generally speaking, a chemical analysis of the chamber gases is not made, and under ordinary working conditions little would be gained from such an analysis, owing to the difficulty of obtaining really average samples; and further, it is unnecessary, since the process can be perfectly controlled by the analysis of the inlet and outlet gases. Should it be desirable in a special and exceptional case to investigate the chamber gases, the methods described for the investigation of the exit gases will be found perfectly satisfactory. For more exact determinations, reference should be made to the methods employed by Lunge and Naef.[1]

The exit gases from the Gay-Lussac tower are in the first place examined for their content in oxygen, which constitutes one of the most important factors for the regulation of the process in general, and for the setting of the damper in the exit flue in particular. In many of the foreign works this estimation is looked upon as sufficient, but in England, and more recently in Germany, in consequence of the legal restrictions imposed, the gases are also tested for total acidity.

1. **Oxygen.**—The oxygen is estimated by absorption, and measuring the resulting decrease in volume. The absorption is effected either by means of an alkaline solution of pyrogallol, which, however, requires to be frequently renewed, and thus involves much time and expense, or preferably by thin rods of moist phosphorus, which allows many hundreds of analyses to be carried out in succession. It must, however, be remembered that phosphorus is not acted upon by oxygen at temperatures below 16°, consequently when the determination has to be made in a cold place, the absorption vessel must be slightly warmed in any convenient manner. Lunge recommends the use of an alkaline solution of sodium hydrosulphite, as suggested by Franzen (*cf.* p. 246), in preference to either of the above reagents for the absorption of oxygen. Since the water with the absorbents will take up any acid gases present, it is necessary to wash the gas by passing it through a solution of sodium hydroxide before proceeding with the absorption of the oxygen.

When, as is usual, it is only necessary to make several single tests in the course of the day, the use of a special aspirator is unnecessary, as the gas burette itself suffices for this purpose by filling and emptying the burette three or four times in succession from the special opening in the gas main; it is then safe to assume that a fair sample of the gas in the main has been collected, and the analysis may be proceeded with.

The practice of making a continuous test, in addition to the above, is strongly to be recommended; that is, to draw the gas slowly during the full twenty-four hours into a special vessel, from which the sample is taken for analysis. For this purpose any suitable aspirator of wood

[1] *Chem. Ind.*, 1884, 7, 5.

or metal may be employed, provided the acid vapours are previously removed from the gases. The apparatus for the estimation of the acids, to be described later, effects this removal very conveniently. On the other hand, more simple appliances may be used, so long as they permit at least 10 litres of the gas to be drawn off and measured in the twenty-four hours, this quantity being essential if a representative average sample is required.

A good form of apparatus, devised by Strype for the investigation of the exit gases, is described and figured in Lunge's *Sulphuric Acid and Alkali*.[1] The apparatus described by Davis,[2] Lovett,[3] and Pringle[4] do not possess any features of special value.

The estimation of oxygen is best carried out by moist phosphorus in an Orsat apparatus (p. 272 *et seq.*), provided with two absorption tubes, the first of which is filled with sodium hydroxide solution to remove the acid gases, and the second with phosphorus. The manipulation is exactly the same as in the examination of chimney gases (p. 275).

Lindemann's apparatus as modified by C. Winkler[5] (Fig. 192) can also be employed. The measuring tube A is fitted above with a three-way tap, and has a capacity of 100 c.c., of which 25 c.c. are contained in the lower cylindrical portion, which is graduated in $\frac{1}{10}$ c.c. B is the absorption vessel filled with thin rods of phosphorus, and C the levelling bottle. The manipulation is the same as in the Orsat apparatus.

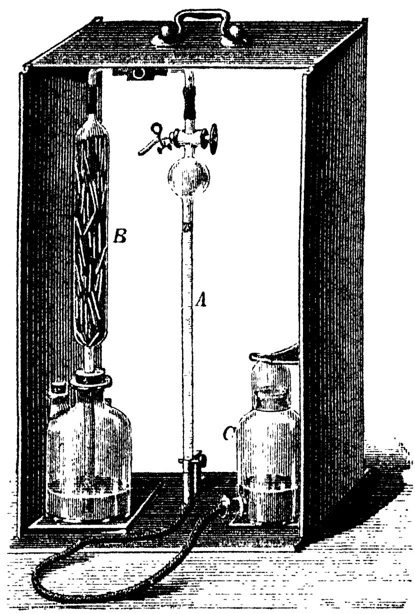

FIG. 192.

M. Liebig's apparatus[6] is arranged for use with alkaline pyrogallol; the gas is aspirated by means of a rubber bellows into a 50 c.c. pipette, and forced from this through the absorbing solution into a graduated measuring tube.

2. Examination for Acids.—If only the sulphur dioxide is to be determined, a measured volume of the exit gas is drawn through sodium hydroxide solution, and the resulting solution, after considerable dilution with water, poured into chlorine or bromine water. This

[1] Vol. i., 4th edition, p. 975.
[2] *Chem. News*, 1880, 41, 188.
[3] *J. Soc. Chem. Ind.*, 1882, 1, 210.
[4] *Ibid.*, 1883, 2, 53.
[5] *Handbook of Technical Gas Analysis*, p. 91.
[6] Post, *Chem. Tech. Analyse*, 2nd edition, 1, p. 700.

solution is then acidified with hydrochloric acid, heated to boiling, and precipitated with barium chloride. Each 1 g. $BaSO_4$ corresponds to 93·75 c.c. SO_2. Reich's method (p. 394) is inapplicable in this case, owing to the disturbing action exerted by the nitrous gases present.

For a complete examination the following directions will suffice. On the one hand the sum of the sulphur acids is determined, and on the other the sum of the nitrogen acids, irrespective of the degree of oxidation. The following scheme agrees in the main with that adopted by the British Alkali Makers' Association in 1878; improvements have, however, been made in some of the analytical details.

A small volume of gas is drawn continuously from the Gay-Lussac exits by means of a constant aspirator, at such a rate that at least 24 cubic feet (0·68 cub. m.) are collected in the twenty-four hours. The volume V drawn off must be measured with sufficient accuracy, either by graduating the aspirator or by means of a gas meter; the volume is then corrected by Tables II. to IV. (Appendix) to 0° and 760 mm., and the corrected volume called V′. To make the comparisons more complete, a record is kept of the number of cubic feet of chamber space for each pound of sulphur burnt and entering the chambers in the twenty-four hours (or kilos sulphur per cubic metre), as calculated from the weekly average; further, of the distance from the tower, of the point at which the samples are taken. The gas is drawn through four absorption bottles, each of 100 c.c. capacity, and giving a column of liquid of at least 75 mm. in depth. The openings of the inlet-tubes may not exceed ½ mm. diameter, as measured by a standard wire. The first three bottles each contain 100 c.c. of normal sodium hydroxide solution (free from nitrate and equal to 31 g. Na_2O per litre), the fourth 100 c.c. of distilled water. The gases are examined for—(1) Total acidity, measured as sulphur trioxide; (2) Sulphur; (3) Nitrogen in the form of acids, both the latter being measured in grains per cubic foot, or g. per cubic metre of the gas (reduced to 0° and 760 mm.). The operation is conducted as follows:—

The contents of the four bottles are combined, the bottles washed out with a small volume of water, and the total divided into three equal parts, one portion being kept as a reserve. The first portion is titrated with normal sulphuric or hydrochloric acid, thus affording a measure of the total acidity, SO_2, H_2SO_4, N_2O_3, and HNO_3. The second portion is added gradually to such quantity of a warm solution of potassium permanganate, rendered strongly acid by means of pure sulphuric acid, that a slight excess of permanganate remains; this excess is finally so far neutralised by a few drops of sulphurous acid solution that only a faint rose tint persists. All the nitrogen acids are now present as nitric acid, and there is no excess of

sulphurous acid in the solution. The nitric acid is estimated by means of ferrous sulphate, employing for the purpose a solution containing 100 g. crystallised ferrous sulphate, and 100 g. pure sulphuric acid per litre. To 25 c.c. of this solution contained in a flask is added a further 20 to 25 c.c. of pure concentrated sulphuric acid, and when the solution is cold the mixture resulting from the above permanganate treatment is poured in. The flask is closed by a stopper furnished with two tubes; the first is connected with a Kipp's apparatus generating carbon dioxide, the second luted in water. The air in the apparatus is expelled by the carbon dioxide, and the contents of the flask heated until the solution, which at the start is dark-coloured owing to the nitric oxide present, has become of a bright yellow colour. This may require from a quarter to one hour according to the quantity of nitric acid present, and the volume of sulphuric acid added. The ferrous salt which remains unoxidised by the nitric acid is titrated back by a $N/2$ permanganate solution equivalent to 0·004 g. oxygen per 1 c.c. (*cf.* p. 59). Since the strength of the acid ferrous sulphate solution alters somewhat rapidly, it is necessary to compare it each day with the permanganate solution by titrating 25 c.c., the quantity taken for the test, with permanganate. If x c.c. of sulphuric acid is used in the first titration, y c.c. of permanganate in titrating back the unoxidised ferrous salt, and z c.c. of permanganate is equivalent to 25 c.c. of the ferrous sulphate solution, the figures required are obtained according to the following equations; the measurement of volume (V′) being of course made in cubic metres or in cubic feet according to the method of expression:—

(1) *Total acidity* expressed in—

Grams SO_3 per cubic metre $= \dfrac{0.120(100 - x)}{V'}$

Grains SO_3 per cubic foot $= \dfrac{1.852(100 - x)}{V'}$

(2) *Sulphur* in—

Grams per cubic metre $= \dfrac{0.008(600 - 6x - z + y)}{V'}$

Grains per cubic foot $= \dfrac{0.12346(600 - 6x - z + y)}{V'}$

(3) *Nitrogen* in—

Grams per cubic metre $= \dfrac{0.007(z - y)}{V'}$

Grains per cubic foot $= \dfrac{0.10803(z - y)}{V'}$

In place of the above method it will often suffice to determine only the total acidity by titrating with $N/10$ sodium hydroxide solution

and phenolphthalein, either according to Lunge's method, described on p. 398, or by employing the ten-bulb tube described below.

The maximum escape allowed under the Alkali Act (1906) equals 4 grains per cubic foot, equivalent to 9·15 g. SO_3 per cubic metre of residual gases, before admixture with air or smoke; in Germany the limit is 5 g. where pyrites is burnt, and 8 g. in the case of blende, all acids being calculated to SO_3.

The alkali inspectors have recently adopted a mixture of 1 vol. $N/2$ alkali and 10 vols. neutral hydrogen peroxide for the absorption of the acid gases. This overcomes the difficulty caused by secondary reactions between sulphites and nitrites which is liable to occur[1] when sodium hydroxide solution is used alone.

3. **Nitric oxide** may always be present in the exit gases even after these have passed through the absorption bottles. Should it be desired to estimate this gas, a ten-bulb absorption tube (Fig. 193) must be placed

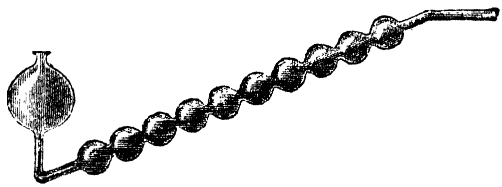

FIG. 193.

between the last flask of the series and the aspirator. The tube is filled with 30 c.c. of $N/2$ potassium permanganate solution to which 1 c.c. of sulphuric acid of sp. gr. 1·25 has been added. After the gas has passed for twenty-four hours the tube is emptied and washed out. Fifty c.c. of ferrous sulphate solution (equivalent to $2z$ c.c. permanganate) is added, and the decolorised solution titrated back with permanganate solution till it again becomes rose-coloured; the number of c.c. of permanganate required is called u. The nitric oxide has thus reduced $(30+u-2z)$ c.c. seminormal permanganate solution. This corresponds to:

$$N = \frac{0.007(30+u-2z)}{3V'}$$

grams nitrogen per cubic metre of the gas when V′ represents the total volume, as registered by the aspirator; or in grains per cubic foot,

$$N = \frac{0.10803(30+u-2z)}{3V'}$$

A Winkler's coil, or other suitable apparatus, may be used instead of the above absorption bulbs.

To test whether all the nitric oxide has been absorbed, Griess'

[1] Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, 21, 1490.

reagent (α-naphthylamine and sulphanilic acid), as modified by Lunge and Ilosvay,[1] may be employed, by allowing air to mix with the gases leaving the bulb-tube, and then examining for higher oxides of nitrogen. The reagent will always show a slight reddening with such gases even where the absorption has been made as complete as possible, but for most practical purposes such traces may be neglected.

According to Divers,[2] a concentrated alkaline solution of sodium or potassium sulphite forms an excellent medium for the absorption of nitric oxide in gas analysis.

Von Knorre and Arndt[3] mix the gas with hydrogen and pass the mixture very slowly through a Drehschmidt platinum capillary tube (p. 257) heated to bright redness. If the gas be passed too quickly or the heating be insufficient, some ammonia always results. The reaction is:

$$\underset{(4\ \text{vols.}}{2NO} + \underset{4\ \text{vols.}}{2H_2} = 2H_2O + \underset{2\ \text{vols.})}{N_2}$$

Consequently each volume of nitric oxide corresponds to a contraction of $1\frac{1}{2}$ volumes.

Von Knorre[4] states that it is more convenient to absorb the nitric oxide in a mixture of 5 volumes of saturated potassium bichromate solution and 1 volume concentrated sulphuric acid than in the acidified permanganate solution described above, since the bichromate mixture is perfectly stable at ordinary temperatures, and does not evolve oxygen when shaken with indifferent gases; further, the nitric oxide is oxidised quantitatively to nitric acid by this mixture. A liberation of absorbed nitric oxide to indifferent gases cannot therefore occur in this case, as it may when ferrous sulphate is employed. This reagent is consequently well adapted for the removal of nitric oxide from mixtures of gases, and also for the estimation of larger amounts of this gas; for the estimation of smaller quantities such as occur in the above cases, absorption in acid permanganate solution and subsequent titration is to be preferred.

4. **Nitrous oxide** in chamber or exit gases has scarcely ever been estimated up to the present. The earlier known method of Winkler,[5] which consists in the removal of the nitrogen acids and oxygen from the gases and conversion of the nitrogen compounds in the residue into ammonia by passing them together with excess of hydrogen over gently heated palladium asbestos, and that of Lunge,[6] which is carried out by first acting upon the gases with concentrated potassium hydroxide solution and permanganate, shaking the residue with absolute alcohol,

[1] *Z. angew. Chem.*, 1890, **3**, 568.
[2] *J. Chem. Soc.*, 1899, **75**, 82.
[3] *Ber.*, 1899, **32**, 2136.
[4] *Chem. Ind.*, 1902, **25**, 534.
[5] *Industrie-Gase*, vol. **2**, p. 429.
[6] *Ber.*, 1881, **14**, 2188.

and decomposing the gases expelled from the alcohol into nitrogen and oxygen by means of a glowing palladium wire, do not suffice where the quantity of nitrous oxide present is so small and is admixed with a largely preponderating amount of nitrogen. The process worked out by Pollak[1] is preferable. The mixture of N_2O (x volumes), NO (y volumes), and N (z volumes), the total observed volume being V, from which all oxygen has previously been removed by means of moist phosphorus, is burnt either with hydrogen or with carbonic oxide in a Drehschmidt tube. The contraction, V_c, is noted, oxygen added to the residual gas, and the mixture again burnt in the capillary. Two-thirds of the resulting contraction is equal to the volume of hydrogen that remains after the first combustion, and this subtracted from the volume of hydrogen originally added gives the volume of hydrogen used, V_w. We thus have:—

$$\begin{aligned}(1)\ & x+y+z = V\\ (2)\ & x+3y/2 = V_c\\ (3)\ & x+y = V_w\end{aligned}$$

from which:—

$$\begin{aligned}x &= 3V_w - 2V_c\\ y &= 2(V_c - V_w)\\ z &= V - V_w\end{aligned}$$

In the case of combustion with carbon monoxide the contraction, V_c, and the carbon dioxide formed, V_k, are measured.

This gives:—

$$\begin{aligned}(1)\ & x+y+z = V\\ (2)\ & y/2 = V_c\\ (3)\ & x+y = V_k\end{aligned}$$

from which it follows:—

$$\begin{aligned}x &= V_k - 2V_c\\ y &= 2V_c\\ z &= V - V_k\end{aligned}$$

5. **Loss of Sulphur.**—Lunge[2] has published a formula which allows the quantity of sulphur burnt, expressed in grams per litre on the exit gases, to be calculated from the percentage volume of oxygen present in these. The sulphur loss may be calculated by comparing this value with the quantity of sulphur acids present in the exit gases. The formula is:

$$x = (20.95 - a)0.009637 \quad \frac{1}{1.00367t} \quad \frac{h}{760}$$

where x equals the total sulphur burnt, expressed in grams per litre on

[1] Treadwell, *Analytical Chemistry*, 5th edition, vol. ii., p. 802. See also Inglis, *J. Soc. Chem. Ind.*, 1904, **23**, 690, 788; 1906, **25**, 149; 1907, **26**, 668.

[2] Cf. *Sulphuric Acid and Alkali*, vol. i., p. 986; *Dingl. polyt. J.*, 1877, **226**, 634.

the exit gas, a the percentage volume of oxygen in the exit gas, t its temperature, and h the pressure.

EXAMINATION OF THE WORKS' ACIDS

The strength of the *Drips* from the chambers is observed at frequent intervals during the day and their content in nitrous vitriol gauged, at least by a rough test. The latter can, of course, be more exactly estimated by means of permanganate solution. Tests of the bottom-acid are also made.

For collecting the "drips" Lunge[1] recommends the use of small cylinders of 20 c.c. capacity and correspondingly small hydrometers having a range of about 20° Tw., in place of the customary larger cylinder and full-range hydrometers. The smaller cylinders have the advantage that the acid is renewed about every ten minutes, and thus show any changes more quickly.

For a rapid, approximate determination of the *Nitrosity* (percentage of nitrogen acids) of the drips, Lunge[2] recommends the following method for testing a set of four chambers. The test should be performed at least once, better twice, daily, and for each test a stand furnished with eight ordinary test tubes, each 13 cm. high, is employed. The test tubes are each filled to a height of 10 cm. with samples of the bottom-acid and of the drip-acid respectively, of each of the chambers, taken in turn. The strength of each sample is taken at the same time by the hydrometer and written on the stand at the bottom of the respective tube. Concentrated ferrous sulphate solution, which does not require to be free from ferric salts, is then cautiously added so as to form a layer about 1 cm. deep on the acid in each cylinder. In the presence of very minute traces of nitric acid or of the lower oxides of nitrogen a yellowish coloured ring results at the junction of the liquids. In the presence of larger amounts of nitrogen acids the ring is darker, or with still greater quantities the whole of the ferrous sulphate layer assumes a deep brown to black colour, and may even begin to froth owing to the heat evolved driving off the dissolved nitric oxide from the solution. By an inspection of the various colours in their sequence from chamber to chamber, coupled with the strength of the acid from each chamber and the colour of the gases in the latter, a very good indication of the operation of the chamber process is obtained. The estimation of the sulphur dioxide in the inlet gases and of the oxygen in the exit gases complete the necessary testing.

The bottom-acid in the first chamber should show no trace of nitrous acid. In the middle chambers the test should indicate a small quantity of nitrous acid in the bottom-acid and a more pronounced

[1] *Sulphuric Acid and Alkali*, vol. i., p. 698. [2] *Ibid.*, p. 929.

quantity in the drips. The bottom-acid in the last chamber should give at least a moderate indication, and the drips a very marked reaction.

Should selenium be present the ferrous sulphate test is not so easily applied; it may, however, be successfully employed after some practice.

For the quantitative estimation of the nitrogen acids in vitriol the potassium bichromate method was formerly generally employed, but it has now been replaced by the permanganate method, which gives a much sharper end-reaction. The details of the permanganate method are given under "Gay-Lussac acid" (see below).

It has been suggested that the daily production of acid might be deduced by measuring the drips from the chambers. Lunge[1] has shown, however, that this view is incorrect, owing to the drip tables acting as contact surfaces. They consequently not only collect the acid normally produced at the point of the chamber considered, but also the much larger volume of acid condensed locally either by mechanical means or owing to a better admixture of, and accompanying reaction in, the chamber gases impinging against the solid wall.

The yield of chamber acid should be determined directly by measuring the acid dip in the chambers, which is done by means of vessels communicating with the interior. It is advisable to draw up a table for each chamber, so as to see at a glance the volume of acid, in cubic feet or litres, corresponding to any observed dip. If the specific gravity be determined at the same time by means of the hydrometer, the weight of acid in the chamber can be calculated.

Examination of the Glover acid. The strength (140° to 150° Tw., sp. gr. 1·7 to 1·75) and temperature are determined in case the acid is to be pumped back at once to the Gay-Lussac tower; also the content in nitrous compounds, should more than traces of these be present. (This determination is described on p. 449.) Other tests are carried out exactly as for the nitrous vitriol from the Gay-Lussac tower.

Examination of the Gay-Lussac acid (Nitrous vitriol). Generally only the nitrous acid is determined; this is not present in the vitriol in the free condition, but is combined to form nitrosyl-sulphuric acid $SO_2(OH)(ONO)$. Nitric acid only occurs in poor nitrous vitriol; it is included in the total nitrogen found by the nitrometer test.

Nitrous acid is usually estimated by the permanganate method; the bichromate method is to-day seldom employed (cf. *supra*). The test is carried out in the manner proposed by Lunge,[2] who has shown that the earlier methods employed were inaccurate, owing to the ready loss of nitric oxide and production of nitric acid that took place before the

[1] *Z. angew. Chem.*, 1889, **2**, 265.
[2] *Ber.*, 1877, **10**, 1075.

reaction with permanganate was effected. A seminormal permanganate solution, prepared and standardised as described (p. 61), is employed. The essential point to be observed is that the nitrous vitriol must always be added to the permanganate, and never the reverse. The test is carried out by allowing the sample to flow from a glass-tap burette into a measured volume of the $N/2$ permanganate solution, diluted with five times its volume of warm water (30° to 40°), until the colour just vanishes. At the ordinary temperature the reaction proceeds too slowly, whilst at too high a temperature or in too concentrated solution hydrated manganese dioxide separates out; such separation gives trouble, but it does not prevent the titration being carried to a finish, since the dioxide goes into solution again before the completion of the titration. The quantity of permanganate taken varies according as the vitriol to be tested contains much or little nitrous acid; 1 c.c. permanganate corresponds to 0·009502 g. N_2O_3. For chamber acid or other similar acid, 5 c.c. of permanganate solution at most are taken; for a strong nitrous vitriol, up to 50 c.c. Should it be desired to express the nitrogen content otherwise than as N_2O_3, the factor 9·502 is substituted by 15·75 for HNO_3 by 29·83 for nitric acid of 66°·5 Tw. at 15°C., by 25·30 for nitric acid of 77° Tw., and by 21·252 for $NaNO_3$.

The following table (p. 414) saves calculation for cases in which 50 c.c. of permanganate solution is employed. The number of c.c. of nitrous vitriol required is given in column y, the content in g. per litre in column a, and in column b the percentage by weight, assuming the acid examined to be of sp. gr. 1·71 (142° Tw.). For other strengths of acid the percentage by weight is found by dividing the values in column a by ten times the specific gravity of the acid.

Riegler[1] has proposed to estimate the nitrous acid by the gas-volumetric method, using hydrogen peroxide according to the reaction:—

$$HNO_2 + H_2O_2 = H_2O + HNO_3$$

and measuring the volumes of oxygen evolved by the action of permanganate on 5 c.c. of the hydrogen peroxide alone, and on 5 c.c. of the peroxide after reaction on a known amount of the acid to be tested.

Grützner[2] estimates the nitrite by determining by Volhard's method (p. 74) the chloride produced by interaction with chloric acid:—

$$3HNO_2 + HClO_3 = 3HNO_3 + HCl.$$

[1] *Z. anal. Chem.*, 1897, 36, 665.
[2] *Arch. Pharm.*, 35, 241.

Table for the estimation of Nitrous Acid in Nitrous Vitriol.

Expressed as HNO_3, $NaNO_3$, and as nitric acid of 66°·5 and 77° Tw. at 15° C., when 50 c.c. *N*/2 potassium permanganate is taken for the titration, and the percentages by weight are based on sulphuric acid of 142° Tw. as unit.

Acid required.	HNO_3.		$NaNO_3$.		Nitric Acid 66°·5 Tw.		Nitric Acid 77° Tw.	
y. c.c.	*a*. G. per Litre.	*b*. Percentage by Weight.	*a*. G. per Litre.	*b* Percentage by Weight.	*a*. G. per Litre.	*b*. Percentage by Weight.	*a*. G. per Litre.	*b*. Percentage by Weight.
10	78·8	4·61	106·3	6·22	149·1	8·72	127·2	7·44
11	71·6	4·19	96·6	5·65	135·6	7·93	115·6	6·76
12	65·6	3·84	88·6	5·18	124·3	7·27	106·0	6·20
13	60·6	3·54	81·8	4·78	111·7	6·70	97·8	5·72
14	56·2	3·29	75·9	4·44	106·5	6·23	90·8	5·31
15	52·5	3·07	70·9	4·14	99·4	5·80	84·8	4·96
16	49·2	2·88	66·4	3·88	93·2	5·45	79·5	4·65
17	46·3	2·71	62·5	3·65	87·7	5·13	74·8	4·37
18	43·7	2·56	59·0	3·45	82·9	4·85	70·7	4·13
19	41·5	2·42	55·9	3·27	78·5	4·59	66·9	3·91
20	39·4	2·30	53·1	3·11	74·6	4·36	63·6	3·72
21	37·5	2·19	50·6	2·96	71·0	4·15	60·6	3·54
22	35·8	2·09	48·3	2·82	67·8	3·96	57·8	3·38
23	34·2	2·00	46·2	2·70	64·8	3·79	55·3	3·23
24	32·8	1·92	44·3	2·60	62·1	3·62	53·0	3·11
25	31·5	1·84	42·5	2·49	59·7	3·49	50·8	2·97
26	30·3	1·77	40·9	2·39	57·4	3·35	48·9	2·86
27	29·2	1·71	39·4	2·30	55·2	3·25	47·1	2·75
28	28·1	1·65	38·0	2·22	53·3	3·12	45·4	2·66
29	27·1	1·59	36·7	2·15	51·4	3·01	43·9	2·56
30	26·3	1·54	35·4	2·07	49·7	2·91	42·4	2·48
31	25·4	1·49	34·3	2·01	48·1	2·81	41·0	2·40
32	24·6	1·44	33·2	1·94	46·6	2·73	39·7	2·32
33	23·9	1·40	32·2	1·88	45·2	2·64	38·5	2·25
34	23·2	1·35	31·3	1·84	43·9	2·56	37·4	2·19
35	22·5	1·32	30·4	1·78	42·6	2·49	36·3	2·13
36	21·9	1·28	29·5	1·73	41·4	2·42	35·3	2·07
37	21·3	1·24	28·7	1·68	40·3	2·36	34·4	2·01
38	20·7	1·21	28·0	1·64	39·3	2·30	33·5	1·96
39	20·2	1·18	27·3	1·60	38·2	2·23	32·6	1·91
40	19·7	1·15	26·5	1·55	37·3	2·18	31·8	1·86
41	19·2	1·12	25·8	1·51	36·4	2·13	31·0	1·81
42	18·8	1·10	25·3	1·48	35·5	2·08	30·3	1·77
43	18·3	1·07	24·7	1·45	34·6	2·02	29·5	1·73
44	17·9	1·05	24·2	1·42	33·9	1·98	28·9	1·69
45	17·5	1·02	23·6	1·38	33·1	1·93	28·2	1·65
46	17·1	1·00	23·1	1·35	32·4	1·90	27·6	1·62
47	16·7	0·98	22·6	1·32	31·7	1·85	27·0	1·58
48	16·4	0·96	22·2	1·30	31·1	1·82	26·5	1·55
49	16·1	0·94	21·7	1·27	30·4	1·78	25·9	1·51
50	15·8	0·921	21·3	1·25	29·8	1·74	25·4	1·49
55	14·3	0·837	19·3	1·13	27·1	1·59	23·1	1·35
60	13·1	0·768	17·7	1·04	24·5	1·45	21·2	1·24
65	12·1	0·709	16·4	0·96	22·9	1·34	19·6	1·14
70	11·2	0·658	15·2	0·89	21·3	1·25	18·2	1·06
75	10·5	0·614	14·17	0·829	19·9	1·16	16·96	0·99
80	9·85	0·576	13·3	0·778	18·6	1·09	15·9	0·93
85	9·2	0·542	12·5	0·731	17·5	1·03	14·9	0·87
90	8·7	0·511	11·8	0·692	16·5	0·967	14·1	0·825
95	8·3	0·485	11·2	0·655	15·7	0·918	13·4	0·783
100	7·9	0·461	10·6	0·620	14·9	0·873	12·7	0·744

The estimation of the total nitrogen acids present in nitrous vitriol is generally effected in the nitrometer, the use of which for this purpose has been already described (p. 79). Should the acid contain, in addition to the nitrous acid, appreciable quantities of sulphur dioxide, which can readily be detected by the smell, a little powdered potassium permanganate is placed in the cup of the nitrometer; a large excess of permanganate must not be used, since it interferes considerably with the reaction.

The observed gas volume must be reduced to 0° and 760 mm. by means of the Tables II. and III. (Appendix), unless the gas-volumeter (*cf.* p. 83) be employed; with the latter instrument it is especially advisable to use a separate decomposition vessel.

The nitrogen compounds are calculated from the corrected nitric oxide volumes by means of the following table. The table takes account of the various ways of stating results adopted in different works, and will be found useful in other than sulphuric acid works. Column *a* gives the values in milligrams throughout, column *b* the percentage by weight, assuming that 1 c.c. of acid of 142° Tw. has been taken for analysis; for other strengths of acid the values under *a* must be taken as the basis for calculation (*cf.* p. 413).

c.c. NO.	N.		NO.		N_2O_3.	
	a. mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.
1	0·6257	0·0366	1·3402	0·0784	1·6975	0·0993
2	1·2514	0·0732	2·6804	0·1568	3·3950	0·1986
3	1·8771	0·1098	4·0206	0·2352	5·0925	0·2979
4	2·5028	0·1464	5·3608	0·3136	6·7900	0·3972
5	3·1385	0·1830	6·7010	0·3920	8·4875	0·4965
6	3·7542	0·2196	8·0412	0·4704	10·1850	0·5958
7	4·3799	0·2562	9·3814	0·5488	11·8825	0·6951
8	5·0056	0·2928	10·7216	0·6272	13·5800	0·7944
9	5·6313	0·3294	12·0618	0·7056	15·2775	0·8937

c.c. NO.	HNO_3.		Nitric Acid 66°·5 Tw.		$NaNO_3$.	
	a. mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.	*a.* mg.	*b.* Percentage.
1	2·8144	0·1646	5·333	0·312	3·7986	0·2221
2	5·6288	0·3292	10·666	0·624	7·5972	0·4442
3	8·4432	0·4938	15·999	0·936	11·3958	0·6663
4	11·2576	0·6584	21·332	1·248	15·1944	0·8884
5	14·0720	0·8230	26·665	1·560	18·9930	1·1105
6	16·8864	0·9876	31·998	1·872	22·7916	1·3326
7	19·7008	1·1522	37·331	2·184	26·5902	1·5547
8	22·5152	1·3168	42·664	2·496	30·3888	1·7768
9	25·3296	1·4814	47·997	2·808	34·1874	1·9989

One hundred parts of nitric acid of 66°·5 Tw. correspond to 71·23 parts pure $NaNO_3$, or 74·20 parts of 96 per cent. Chili saltpetre.

The other methods described under "Nitrating and Spent Acids" (p. 497) may also be used for this determination.

Ratios of the nitrogen compounds to each other. The following formulæ may be used to determine the relationships among the N_2O_3, N_2O_4, and HNO_3, present together in sulphuric acid, when the results of the permanganate titration and the nitrometer determination of total nitrogen in the form of NO are known:—

a = c.c. NO, as found in the nitrometer;

b = c.c. O, calculated from the permanganate titration (1 c.c. O = 1·4278 mg., consequently 1 c.c. $N/2$ permanganate = 0·004 g. = 2·8015 c.c. oxygen);

x = vol. NO, corresponding to N present as N_2O_3;

y = vol. NO, „ „ N_2O_4;

z = vol. NO, „ „ HNO_3.

If $4b > a$, then:—

$$x = 4b - a\ ;\ y = 2(a - 2b) \text{ or } = a - x.$$

If $4b < a$, then:—

$$y = 4b\ ;\ z = a - 4b.$$

That is, if the oxygen is sufficient to allow of all the nitrogen acids being present as N_2O_4, they are calculated as such; if there is more than sufficient oxygen for this the excess is calculated to HNO_3, whilst if there is less oxygen the deficit is calculated to N_2O_3. In practice, the ordinary nitrous vitriol contains no N_2O_4, on which account it is better to calculate the total oxygen deficit (as determined by permanganate) to N_2O_3 or to nitrosyl-sulphuric acid, the rest of the nitrogen being calculated to nitric acid.

Finished Product: Sulphuric Acid

Sulphuric acid appears in commerce as chamber acid of 106° to 116° Tw.; as 140° Tw. acid from the Glover tower, or after evaporation in lead pans; as ordinary 168° Tw. acid (93 to 95 per cent.); as extra concentrated acid (96 to 98 per cent.); as commercial monohydrate, and as fuming sulphuric acid. The last will be dealt with separately.

Actual sulphuric acid, generally referred to as monohydrate, H_2SO_4, has a specific gravity of 1·853 at 0° and, according to different observers, of 1·8372 to 1·8384 at 15° compared with water at 4°. The German Standards Commission calculate the specific gravity of actual monohydrate as 1·8357 at 15°/4° by extrapolation; it should, however, be borne in mind that this extraordinarily low value is doubtful, as owing to the remarkable irregularities that occur in the density curve when such high concentrations are reached extrapolation may be very

misleading. The maximum specific gravity (1·8415) lies between 97 and 98 per cent. acid, and the density of the monohydrate is thus increased by addition of a little water as well as by addition of sulphuric anhydride. The monohydrate begins to boil at 290°, and at first evolves some SO_3, the boiling point rising to 338°, at which temperature 98 per cent. of H_2SO_4 and 2 per cent. of H_2O are present.[1]

The strength of sulphuric acid is generally determined by its specific gravity. The earlier tables in use have been found to be altogether unreliable, especially at the higher concentrations, and Lunge and Isler[2] consequently worked out a new table based on fresh observations, using, however, the values previously determined by Lunge and Naef[3] for acids of over 90 per cent. H_2SO_4. All uncertainty in this connection has now been removed by the very exhaustive and painstaking investigations of Domke, Bein, Fischer, and others, whose work is embodied in the reports of the German Standards Commission.[4] This work, undertaken in the first place for the establishment of the normals for percentage hydrometers, has been carried out with such care that the results may safely be looked upon as exact; the report contains in addition a detailed description and criticism of all previous work on the subject.

The following tables are taken from this source. (1) The table for the estimation of the sp. gr. (15° C./4° C.) of pure sulphuric acid and water mixtures from the percentage content; the fifth decimal place, which was only determined for purposes of calculation, is omitted, but has been used to round off the fourth figure. (2) An extract from the tables for reducing to 15° C. the reading found at some other temperature. The original memoir contains many other tables of less importance for the present purpose which are not included here.

In these tables the values are given for progressively increasing percentages of sulphuric acid. The form adopted in the tables prepared by Lunge, based upon measurements made in conjunction with Isler and Naef, is much more useful for works and laboratory purposes. These tables are accordingly included; they have been recalculated to the values of the German Standards Commission wherever they differed by more than 0·1 per cent. Larger variations than this scarcely appear below the specific gravity of 1·560, but between this point and 1·680 differences rising up to about ¾ per cent. occur; the causes of these divergencies have not yet been discovered. Still greater differences exist at certain of the higher concentrations, especially from 96 per cent. onwards, but at these strengths the determination of the acid content by means of the specific gravity

[1] *Cf.* W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, 1923, p. 194.

[2] *Z. angew. Chem.*, 1890, **3**, 131.

[3] *Chem. Ind.*, 1883, **6**, 37.

[4] *Abhandlungen*, 1904, vol. 5.

is quite unreliable, and consequently the readings do not come into question for practical purposes. Perhaps the most pronounced variation (0·54 per cent.) occurs at 99½ per cent., and it is interesting to note that Koechlin and Gerber have shown that at this extremely high concentration acids prepared in different ways may, although of the same chemical composition, possess different physical properties, a view hinted at by Lunge in 1883. A greater degree of accuracy than 0·1 per cent. is not likely to be attained in practice, and this limit is more than sufficient for the tables, since the figures given are for chemically pure acid which is not found in ordinary practical work. It may be noted that the German Standards Commission always worked to temperatures as recorded by the hydrogen scale, which at 15° gives values 0·1° lower than those recorded on the mercury scale.

Table for determining the Specific Gravity of Pure Sulphuric Acid-water Mixtures from the Percentage Content.

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
0	0·9991	0·9998	1·0005	1·0012	1·0019	1·0026	1·0033	1·0040	1·0047	1·0054
1	1·0061	1·0068	1·0079	1·0082	1·0088	1·0095	1·0102	1·0109	1·0116	1·0122
2	1·0129	1·0136	1·0143	1·0149	1·0156	1·0163	1·0170	1·0176	1·0183	1·0190
3	1·0197	1·0203	1·0210	1·0217	1·0224	1·0230	1·0237	1·0244	1·0251	1·0257
4	1·0264	1·0271	1·0277	1·0284	1·0291	1·0298	1·0304	1·0311	1·0318	1·0325
5	1·0332	1·0338	1·0345	1·0352	1·0359	1·0366	1·0373	1·0380	1·0386	1·0393
6	1·0400	1·0407	1·0414	1·0421	1·0428	1·0435	1·0442	1·0449	1·0456	1·0462
7	1·0469	1·0476	1·0483	1·0490	1·0497	1·0504	1·0511	1·0518	1·0525	1·0532
8	1·0539	1·0546	1·0554	1·0561	1·0568	1·0575	1·0582	1·0589	1·0596	1·0603
9	1·0610	1·0617	1·0624	1·0631	1·0638	1·0645	1·0653	1·0660	1·0667	1·0674
10	1·0681	1·0688	1·0695	1·0702	1·0710	1·0717	1·0724	1·0731	1·0738	1·0745
11	1·0753	1·0760	1·0767	1·0774	1·0781	1·0789	1·0796	1·0803	1·0810	1·0818
12	1·0825	1·0832	1·0839	1·0847	1·0854	1·0861	1·0868	1·0876	1·0883	1·0890
13	1·0898	1·0905	1·0912	1·0920	1·0927	1·0934	1·0942	1·0949	1·0956	1·0964
14	1·0971	1·0978	1·0986	1·0993	1·1000	1·1008	1·1015	1·1023	1·1030	1·1038
15	1·1045	1·1052	1·1060	1·1067	1·1075	1·1082	1·1090	1·1097	1·1105	1·1112
16	1·1120	1·1127	1·1135	1·1142	1·1150	1·1157	1·1165	1·1172	1·1180	1·1187
17	1·1195	1·1202	1·1210	1·1217	1·1225	1·1233	1·1240	1·1248	1·1255	1·1263
18	1·1270	1·1278	1·1286	1·1293	1·1301	1·1309	1·1316	1·1324	1·1331	1·1339
19	1·1347	1·1354	1·1362	1·1370	1·1377	1·1385	1·1393	1·1400	1·1408	1·1416
20	1·1424	1·1431	1·1439	1·1447	1·1454	1·1462	1·1470	1·1478	1·1485	1·1493
21	1·1501	1·1509	1·1516	1·1524	1·1532	1·1540	1·1548	1·1555	1·1563	1·1571
22	1·1579	1·1587	1·1594	1·1602	1·1610	1·1618	1·1626	1·1634	1·1641	1·1649
23	1·1657	1·1665	1·1673	1·1681	1·1689	1·1697	1·1705	1·1712	1·1720	1·1728
24	1·1736	1·1744	1·1752	1·1760	1·1768	1·1776	1·1784	1·1792	1·1800	1·1808

Specific Gravity of Pure Sulphuric Acid-water—*Continued.*

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
25	1·1816	1·1824	1·1832	1·1840	1·1848	1·1856	1·1864	1·1872	1·1880	1·1888
26	1·1896	1·1904	1·1912	1·1920	1·1928	1·1936	1·1944	1·1952	1·1960	1·1968
27	1·1976	1·1984	1·1992	1·2000	1·2008	1·2016	1·2025	1·2033	1·2041	1·2049
28	1·2057	1·2065	1·2073	1·2081	1·2089	1·2098	1·2106	1·2114	1·2122	1·2130
29	1·2138	1·2146	1·2155	1·2163	1·2171	1·2179	1·2187	1·2196	1·2204	1·2212
30	1·2220	1·2228	1·2237	1·2245	1·2253	1·2261	1·2270	1·2278	1·2286	1·2294
31	1·2302	1·2311	1·2319	1·2327	1·2335	1·2344	1·2352	1·2360	1·2368	1·2377
32	1·2385	1·2393	1·2402	1·2410	1·2418	1·2426	1·2435	1·2443	1·2451	1·2460
33	1·2468	1·2476	1·2485	1·2493	1·2501	1·2510	1·2518	1·2526	1·2535	1·2543
34	1·2552	1·2560	1·2568	1·2577	1·2585	1·2594	1·2602	1·2610	1·2619	1·2627
35	1·2636	1·2644	1·2653	1·2661	1·2670	1·2678	1·2686	1·2695	1·2703	1·2712
36	1·2720	1·2729	1·2737	1·2746	1·2754	1·2763	1·2771	1·2780	1·2788	1·2797
37	1·2806	1·2814	1·2823	1·2831	1·2840	1·2848	1·2857	1·2866	1·2874	1·2883
38	1·2891	1·2900	1·2909	1·2917	1·2926	1·2935	1·2943	1·2952	1·2961	1·2969
39	1·2978	1·2987	1·2995	1·3004	1·3013	1·3022	1·3030	1·3039	1·3048	1·3057
40	1·3065	1·3074	1·3083	1·3092	1·3101	1·3109	1·3118	1·3127	1·3136	1·3145
41	1·3153	1·3162	1·3171	1·3180	1·3189	1·3198	1·3207	1·3215	1·3224	1·3233
42	1·3242	1·3251	1·3260	1·3269	1·3278	1·3287	1·3296	1·3305	1·3314	1·3323
43	1·3332	1·3341	1·3350	1·3359	1·3368	1·3377	1·3386	1·3395	1·3404	1·3413
44	1·3423	1·3432	1·3441	1·3450	1·3459	1·3468	1·3478	1·3487	1·3496	1·3505
45	1·3514	1·3524	1·3533	1·3542	1·3551	1·3561	1·3570	1·3579	1·3589	1·3598
46	1·3607	1·3617	1·3626	1·3635	1·3645	1·3654	1·3664	1·3673	1·3682	1·3692
47	1·3701	1·3711	1·3720	1·3730	1·3739	1·3749	1·3758	1·3768	1·3777	1·3787
48	1·3796	1·3806	1·3816	1·3825	1·3835	1·3844	1·3854	1·3864	1·3873	1·3883
49	1·3893	1·3902	1·3912	1·3922	1·3931	1·3941	1·3951	1·3961	1·3970	1·3980
50	1·3990	1·4000	1·4010	1·4019	1·4029	1·4039	1·4049	1·4059	1·4069	1·4079
51	1·4088	1·4098	1·4108	1·4118	1·4128	1·4138	1·4148	1·4158	1·4168	1·4178
52	1·4188	1·4198	1·4208	1·4218	1·4228	1·4238	1·4249	1·4259	1·4269	1·4279
53	1·4289	1·4299	1·4309	1·4319	1·4330	1·4340	1·4350	1·4360	1·4370	1·4381
54	1·4391	1·4401	1·4411	1·4422	1·4432	1·4442	1·4453	1·4463	1·4473	1·4484
55	1·4494	1·4504	1·4515	1·4525	1·4535	1·4546	1·4556	1·4567	1·4577	1·4587
56	1·4598	1·4608	1·4619	1·4629	1·4640	1·4650	1·4661	1·4671	1·4682	1·4692
57	1·4703	1·4714	1·4724	1·4735	1·4745	1·4756	1·4767	1·4777	1·4788	1·4798
58	1·4809	1·4820	1·4831	1·4841	1·4852	1·4863	1·4873	1·4884	1·4895	1·4905
59	1·4916	1·4927	1·4938	1·4949	1·4960	1·4970	1·4981	1·4992	1·5003	1·5013
60	1·5024	1·5035	1·5046	1·5057	1·5068	1·5079	1·5090	1·5101	1·5112	1·5122
61	1·5133	1·5144	1·5155	1·5166	1·5177	1·5188	1·5199	1·5210	1·5221	1·5232
62	1·5243	1·5254	1·5265	1·5276	1·5287	1·5298	1·5309	1·5321	1·5332	1·5343
63	1·5354	1·5365	1·5376	1·5387	1·5398	1·5410	1·5421	1·5432	1·5443	1·5454
64	1·5465	1·5477	1·5488	1·5499	1·5510	1·5521	1·5533	1·5544	1·5555	1·5566
65	1·5578	1·5589	1·5600	1·5612	1·5623	1·5634	1·5645	1·5657	1·5668	1·5679
66	1·5691	1·5702	1·5713	1·5725	1·5736	1·5748	1·5759	1·5770	1·5782	1·5793
67	1·5805	1·5816	1·5827	1·5839	1·5850	1·5862	1·5873	1·5885	1·5896	1·5908
68	1·5919	1·5931	1·5942	1·5954	1·5965	1·5977	1·5989	1·6000	1·6012	1·6023
69	1·6035	1·6046	1·6058	1·6070	1·6081	1·6093	1·6104	1·6116	1·6128	1·6139

Specific Gravity of Pure Sulphuric Acid-water—*Continued.*

Per cent. Sulphuric Acid.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
	Density of Sulphuric Acid at +15° C. compared with Water at +4° C. for percentages given in units in the vertical column at the side, and in decimal parts in the horizontal line above.									
70	1·6151	1·6163	1·6174	1·6186	1·6198	1·6209	1·6221	1·6233	1·6245	1·6256
71	1·6268	1·6280	1·6291	1·6303	1·6315	1·6327	1·6338	1·6350	1·6362	1·6374
72	1·6385	1·6397	1·6409	1·6421	1·6433	1·6444	1·6456	1·6468	1·6480	1·6492
73	1·6503	1·6515	1·6527	1·6539	1·6551	1·6563	1·6574	1·6586	1·6598	1·6610
74	1·6622	1·6634	1·6645	1·6657	1·6669	1·6681	1·6693	1·6705	1·6717	1·6728
75	1·6740	1·6752	1·6764	1·6776	1·6788	1·6799	1·6811	1·6823	1·6835	1·6847
76	1·6858	1·6870	1·6882	1·6894	1·6906	1·6917	1·6929	1·6941	1·6953	1·6965
77	1·6976	1·6988	1·7000	1·7012	1·7023	1·7035	1·7047	1·7058	1·7070	1·7082
78	1·7093	1·7105	1·7117	1·7128	1·7140	1·7151	1·7163	1·7175	1·7186	1·7198
79	1·7209	1·7221	1·7232	1·7244	1·7255	1·7267	1·7278	1·7289	1·7301	1·7312
80	1·7324	1·7335	1·7346	1·7357	1·7369	1·7380	1·7391	1·7402	1·7413	1·7424
81	1·7435	1·7446	1·7457	1·7468	1·7479	1·7490	1·7501	1·7512	1·7523	1·7534
82	1·7544	1·7555	1·7566	1·7576	1·7587	1·7597	1·7608	1·7618	1·7628	1·7639
83	1·7649	1·7659	1·7669	1·7679	1·7689	1·7699	1·7709	1·7719	1·7729	1·7738
84	1·7748	1·7758	1·7767	1·7777	1·7786	1·7796	1·7805	1·7814	1·7823	1·7832
85	1·7841	1·7850	1·7859	1·7868	1·7876	1·7885	1·7894	1·7902	1·7911	1·7919
86	1·7927	1·7935	1·7943	1·7951	1·7959	1·7967	1·7975	1·7983	1·7991	1·7998
87	1·8006	1·8013	1·8021	1·8028	1·8035	1·8042	1·8049	1·8056	1·8063	1·8070
88	1·8077	1·8084	1·8090	1·8097	1·8103	1·8110	1·8116	1·8122	1·8129	1·8135
89	1·8141	1·8147	1·8153	1·8158	1·8164	1·8170	1·8176	1·8181	1·8187	1·8192
90	1·8198	1·8203	1·8208	1·8213	1·8219	1·8224	1·8229	1·8234	1·8239	1·8244
91	1·8248	1·8253	1·8258	1·8262	1·8267	1·8271	1·8276	1·8280	1·8284	1·8289
92	1·8293	1·8297	1·8301	1·8305	1·8309	1·8313	1·8317	1·8320	1·8324	1·8328
93	1·8331	1·8335	1·8338	1·8341	1·8345	1·8348	1·8351	1·8354	1·8357	1·8360
94	1·8363	1·8366	1·8369	1·8371	1·8374	1·8376	1·8379	1·8381	1·8384	1·8386
95	1·8388	1·8390	1·8392	1·8394	1·8396	1·8398	1·8400	1·8401	1·8403	1·8404
96	1·8406	1·8407	1·8408	1·8409	1·8410	1·8411	1·8412	1·8413	1·8414	1·8414
97	1·8414	1·8415	1·8415	1·8415	1·8415	1·8415	1·8414	1·8414	1·8413	1·8412
98	1·8411	1·8410	1·8409	1·8408	1·8406	1·8405	1·8403	1·8401	1·8398	1·8396
99	1·8393	1·8391	1·8388	1·8385	1·8381	1·8378	(1·8374)	(1·8370)	(1·8366)	(1·8362)
100	(1·8357)	...	...	...	...	...	...	...	...	...

(The values in parentheses from 99·6 to 100 per cent. are extrapolated.)

Specific Gravity of Sulphuric Acid Solutions. Lunge, Isler, and Naef.

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·000	0	0	0·07	0·09	0·12	0·14	0·001	0·001	0·001	0·001
1·005	0·7	1	0·77	0·95	1·21	1·52	0·008	0·009	0·013	0·015
1·010	1·4	2	1·28	1·57	2·01	2·51	0·013	0·016	0·020	0·025
1·015	2·1	3	1·88	2·30	2·95	3·68	0·019	0·023	0·030	0·037
1·020	2·7	4	2·47	3·03	3·88	4·85	0·025	0·031	0·040	0·050
1·025	3·4	5	3·07	3·76	4·82	6·02	0·032	0·039	0·049	0·062
1·030	4·1	6	3·67	4·49	5·78	7·18	0·038	0·046	0·059	0·074
1·035	4·7	7	4·27	5·23	6·73	8·37	0·044	0·054	0·070	0·087
1·040	5·4	8	4·87	5·96	7·64	9·54	0·051	0·062	0·079	0·099
1·045	6·0	9	5·45	6·67	8·55	10·67	0·057	0·071	0·089	0·112
1·050	6·7	10	6·02	7·37	9·44	11·79	0·063	0·077	0·099	0·124
1·055	7·4	11	6·59	8·07	10·34	12·91	0·070	0·085	0·109	0·136
1·060	8·0	12	7·16	8·77	11·24	14·03	0·076	0·093	0·119	0·149
1·065	8·7	13	7·73	9·47	12·14	15·15	0·082	0·102	0·129	0·161
1·070	9·4	14	8·32	10·19	13·05	16·30	0·089	0·109	0·140	0·174
1·075	10·0	15	8·90	10·90	13·96	17·44	0·096	0·117	0·150	0·188
1·080	10·6	16	9·47	11·60	14·87	18·56	0·103	0·125	0·161	0·201
1·085	11·2	17	10·04	12·30	15·76	19·68	0·109	0·133	0·171	0·213
1·090	11·9	18	10·60	12·99	16·65	20·78	0·116	0·142	0·181	0·227
1·095	12·4	19	11·16	13·67	17·52	21·87	0·122	0·150	0·192	0·240
1·100	13·0	20	11·71	14·35	18·39	22·96	0·129	0·158	0·202	0·253
1·105	13·6	21	12·27	15·03	19·26	24·05	0·136	0·166	0·212	0·265
1·110	14·2	22	12·82	15·71	20·13	25·14	0·143	0·175	0·223	0·279
1·115	14·9	23	13·36	16·36	20·96	26·18	0·149	0·183	0·234	0·292
1·120	15·4	24	13·89	17·01	21·80	27·22	0·156	0·191	0·245	0·305
1·125	16·0	25	14·42	17·66	22·63	28·26	0·162	0·199	0·255	0·318
1·130	16·5	26	14·95	18·31	23·47	29·30	0·169	0·207	0·265	0·331
1·135	17·1	27	15·48	18·96	24·29	30·34	0·176	0·215	0·276	0·344
1·140	17·7	28	16·01	19·61	25·13	31·38	0·183	0·223	0·287	0·358
1·145	18·3	29	16·54	20·26	25·96	32·42	0·189	0·231	0·297	0·371
1·150	18·8	30	17·07	20·91	26·79	33·46	0·196	0·239	0·308	0·385
1·155	19·3	31	17·59	21·55	27·61	34·48	0·203	0·248	0·319	0·398
1·160	19·8	32	18·11	22·19	28·43	35·50	0·210	0·257	0·330	0·412
1·165	20·3	33	18·64	22·83	29·25	36·53	0·217	0·266	0·341	0·426
1·170	20·9	34	19·16	23·47	30·07	37·55	0·224	0·275	0·352	0·439
1·175	21·4	35	19·69	24·12	30·90	38·59	0·231	0·283	0·363	0·453
1·180	22·0	36	20·21	24·76	31·73	39·62	0·238	0·292	0·374	0·467
1·185	22·5	37	20·73	25·40	32·55	40·64	0·246	0·301	0·386	0·481
1·190	23·0	38	21·26	26·04	33·37	41·66	0·253	0·310	0·397	0·496
1·195	23·5	39	21·78	26·68	34·19	42·69	0·260	0·319	0·409	0·511
1·200	24·0	40	22·30	27·32	35·01	43·71	0·268	0·328	0·420	0·525
1·205	24·5	41	22·82	27·95	35·83	44·72	0·275	0·337	0·432	0·539
1·210	25·0	42	23·33	28·58	36·66	45·73	0·282	0·346	0·444	0·553
1·215	25·5	43	23·84	29·21	37·45	46·74	0·290	0·355	0·456	0·568
1·220	26·0	44	24·36	29·84	38·23	47·74	0·297	0·364	0·466	0·583
1·225	26·4	45	24·88	30·48	39·05	48·77	0·305	0·373	0·478	0·598
1·230	26·9	46	25·39	31·11	39·86	49·78	0·312	0·382	0·490	0·612
1·235	27·4	47	25·88	31·70	40·61	50·72	0·320	0·391	0·502	0·626
1·240	27·9	48	26·35	32·28	41·37	51·65	0·327	0·400	0·513	0·640
1·245	28·4	49	26·83	32·86	42·11	52·58	0·334	0·409	0·524	0·655
1·250	28·8	50	27·29	33·43	42·84	53·49	0·341	0·418	0·535	0·669
1·255	29·3	51	27·76	34·00	43·57	54·40	0·348	0·426	0·547	0·683
1·260	29·7	52	28·22	34·57	44·30	55·31	0·356	0·435	0·558	0·697
1·265	30·2	53	28·69	35·14	45·03	56·22	0·363	0·444	0·570	0·711

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at 15°/4° (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·270	30·6	54	29·15	35·71	45·76	57·14	0·370	0·454	0·582	0·725
1·275	31·1	55	29·62	36·29	46·50	58·06	0·377	0·462	0·593	0·740
1·280	31·5	56	30·10	36·87	47·24	58·99	0·385	0·472	0·605	0·755
1·285	32·0	57	30·57	37·45	47·99	59·92	0·393	0·481	0·617	0·770
1·290	32·4	58	31·04	38·03	48·73	60·85	0·400	0·490	0·629	0·785
1·295	32·8	59	31·52	38·61	49·47	61·78	0·408	0·500	0·641	0·800
1·300	33·3	60	31·99	39·19	50·21	62·70	0·416	0·510	0·653	0·815
1·305	33·7	61	32·46	39·77	50·96	63·63	0·424	0·519	0·665	0·830
1·310	34·2	62	32·94	40·35	51·71	64·56	0·432	0·529	0·677	0·845
1·315	34·6	63	33·41	40·93	52·45	65·45	0·439	0·538	0·689	0·860
1·320	35·0	64	33·88	41·50	53·18	66·40	0·447	0·548	0·702	0·876
1·325	35·4	65	34·35	42·08	53·92	67·33	0·455	0·557	0·714	0·892
1·330	35·8	66	34·80	42·66	54·67	68·26	0·462	0·567	0·727	0·908
1·335	36·2	67	35·27	43·20	55·36	69·12	0·471	0·577	0·739	0·923
1·340	36·6	68	35·71	43·74	56·05	69·98	0·479	0·586	0·751	0·938
1·345	37·0	69	36·14	44·28	56·74	70·85	0·486	0·596	0·763	0·953
1·350	37·4	70	36·58	44·82	57·43	71·71	0·494	0·605	0·775	0·968
1·355	37·8	71	37·02	45·35	58·11	72·56	0·502	0·614	0·787	0·983
1·360	38·2	72	37·45	45·88	58·79	73·41	0·509	0·624	0·800	0·998
1·365	38·6	73	37·89	46·41	59·48	74·26	0·517	0·633	0·812	1·014
1·370	39·0	74	38·32	46·94	60·15	75·10	0·525	0·643	0·824	1·029
1·375	39·4	75	38·75	47·47	60·83	75·95	0·533	0·653	0·836	1·044
1·380	39·8	76	39·18	48·00	61·51	76·80	0·541	0·662	0·849	1·060
1·385	40·1	77	39·62	48·53	62·19	77·65	0·549	0·672	0·861	1·075
1·390	40·5	78	40·05	49·06	62·87	78·50	0·557	0·682	0·873	1·091
1·395	40·8	79	40·48	49·59	63·55	79·34	0·564	0·692	0·886	1·107
1·400	41·2	80	40·91	50·11	64·21	80·18	0·573	0·702	0·899	1·123
1·405	41·6	81	41·33	50·63	64·88	81·01	0·581	0·711	0·912	1·138
1·410	42·0	82	41·76	51·15	65·55	81·86	0·589	0·721	0·924	1·154
1·415	42·3	83	42·17	51·66	66·21	82·66	0·597	0·730	0·937	1·170
1·420	42·7	84	42·57	52·15	66·82	83·44	0·604	0·740	0·949	1·185
1·425	43·1	85	42·96	52·63	67·44	84·21	0·612	0·750	0·961	1·200
1·430	43·4	86	43·36	53·11	68·06	84·98	0·620	0·759	0·973	1·215
1·435	43·8	87	43·75	53·59	68·68	85·74	0·628	0·769	0·986	1·230
1·440	44·1	88	44·14	54·07	69·29	86·51	0·636	0·779	0·998	1·246
1·445	44·4	89	44·53	54·55	69·90	87·28	0·643	0·789	1·010	1·261
1·450	44·8	90	44·92	55·03	70·52	88·05	0·651	0·798	1·023	1·277
1·455	45·1	91	45·31	55·50	71·12	88·80	0·659	0·808	1·035	1·292
1·460	45·4	92	45·69	55·97	71·72	89·55	0·667	0·817	1·047	1·307
1·465	45·8	93	46·07	56·43	72·31	90·29	0·675	0·827	1·059	1·323
1·470	46·1	94	46·45	56·90	72·91	91·04	0·683	0·837	1·072	1·338
1·475	46·4	95	46·83	57·37	73·51	91·79	0·691	0·846	1·084	1·354
1·480	46·8	96	47·21	57·83	74·10	92·53	0·699	0·856	1·097	1·370
1·485	47·1	97	47·57	58·28	74·68	93·25	0·707	0·865	1·109	1·385
1·490	47·4	98	47·95	58·74	75·27	93·98	0·715	0·876	1·122	1·400
1·495	47·8	99	48·34	59·22	75·88	94·75	0·723	0·885	1·134	1·417
1·500	48·1	100	48·73	59·70	76·50	95·52	0·731	0·896	1·147	1·433
1·505	48·4	101	49·12	60·18	77·12	96·29	0·739	0·906	1·160	1·449
1·510	48·7	102	49·51	60·65	77·72	97·04	0·748	0·916	1·174	1·465
1·515	49·0	103	49·89	61·12	78·32	97·79	0·756	0·926	1·187	1·481
1·520	49·4	104	50·28	61·59	78·93	98·54	0·764	0·936	1·199	1·498
1·525	49·7	105	50·66	62·06	79·52	99·30	0·773	0·946	1·213	1·514
1·530	50·0	106	51·04	62·53	80·13	100·05	0·781	0·957	1·226	1·531
1·535	50·3	107	51·43	63·00	80·73	100·80	0·789	0·967	1·239	1·547
1·540	50·6	108	51·78	63·43	81·28	101·49	0·797	0·977	1·252	1·563

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at $\frac{15°}{4°}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·545	50·9	109	52·12	63·85	81·81	102·16	0·805	0·987	1·264	1·579
1·550	51·2	110	52·46	64·26	82·34	102·82	0·813	0·996	1·276	1·593
1·555	51·5	111	52·79	64·67	82·87	103·47	0·821	1·006	1·289	1·609
1·560	51·8	112	53·22	65·20	83·50	104·30	0·830	1·017	1·303	1·627
1·565	52·1	113	53·59	65·65	84·08	105·03	0·839	1·027	1·316	1·644
1·570	52·4	114	53·95	66·09	84·64	105·73	0·847	1·038	1·329	1·660
1·575	52·7	115	54·32	66·53	85·21	106·42	0·856	1·048	1·343	1·677
1·580	53·0	116	54·65	66·95	85·78	107·10	0·864	1·058	1·356	1·692
1·585	53·3	117	55·03	67·40	86·34	107·85	0·872	1·068	1·369	1·709
1·590	53·6	118	55·37	67·83	86·88	108·52	0·880	1·078	1·382	1·726
1·595	53·9	119	55·73	68·26	87·44	109·21	0·889	1·089	1·395	1·742
1·600	54·1	120	56·09	68·70	88·00	109·92	0·897	1·099	1·409	1·759
1·605	54·4	121	56·44	69·13	88·55	110·61	0·906	1·110	1·422	1·775
1·610	54·7	122	56·79	69·56	89·10	111·30	0·914	1·120	1·435	1·792
1·615	55·0	123	57·15	70·00	89·66	112·00	0·923	1·131	1·449	1·810
1·620	55·2	124	57·49	70·42	90·20	112·68	0·931	1·141	1·462	1·825
1·625	55·5	125	57·84	70·85	90·74	113·35	0·940	1·151	1·473	1·842
1·630	55·8	126	58·18	71·27	91·29	114·02	0·948	1·162	1·489	1·859
1·635	56·0	127	58·53	71·70	91·83	114·71	0·957	1·172	1·502	1·875
1·640	56·3	128	58·88	72·12	92·38	115·40	0·966	1·182	1·516	1·892
1·645	56·6	129	59·22	72·55	92·92	116·06	0·975	1·193	1·529	1·909
1·650	56·9	130	59·57	72·96	93·45	116·72	0·983	1·204	1·543	1·926
1·655	57·1	131	59·92	73·40	94·02	117·44	0·992	1·215	1·557	1·944
1·660	57·4	132	60·26	73·81	94·54	118·11	1·000	1·225	1·570	1·960
1·665	57·7	133	60·61	74·24	95·08	118·77	1·009	1·230	1·584	1·977
1·670	57·9	134	60·95	74·66	95·62	119·36	1·017	1·246	1·598	1·995
1·675	58·2	135	61·29	75·08	96·16	120·11	1·027	1·259	1·611	2·012
1·680	58·4	136	61·63	75·50	96·69	120·50	1·035	1·268	1·625	2·029
1·685	58·7	137	61·93	75·94	97·21	121·38	1·043	1·278	1·638	2·046
1·690	58·9	138	62·29	76·38	97·77	122·08	1·053	1·289	1·652	2·064
1·695	59·2	139	62·64	76·76	98·32	122·77	1·062	1·301	1·667	2·082
1·700	59·5	140	63·00	77·17	98·89	123·47	1·071	1·312	1·681	2·100
1·705	59·7	141	63·35	77·60	99·44	124·16	1·080	1·323	1·696	2·117
1·710	60·0	142	63·70	78·04	100·00	124·86	1·089	1·334	1·710	2·136
1·715	60·2	143	64·07	78·48	100·56	125·57	1·099	1·346	1·725	2·154
1·720	60·4	144	64·43	78·92	101·13	126·27	1·108	1·357	1·739	2·172
1·725	60·6	145	64·78	79·36	101·69	126·98	1·118	1·369	1·754	2·191
1·730	60·9	146	65·14	79·80	102·25	127·68	1·127	1·381	1·769	2·209
1·735	61·1	147	65·50	80·24	102·82	128·38	1·136	1·392	1·784	2·228
1·740	61·4	148	65·86	80·68	103·38	129·09	1·146	1·404	1·799	2·247
1·745	61·6	149	66·22	81·12	103·95	129·79	1·156	1·416	1·814	2·265
1·750	61·8	150	66·58	81·56	104·52	130·49	1·165	1·427	1·829	2·284
1·755	62·1	151	66·94	82·00	105·08	131·20	1·175	1·439	1·845	2·303
1·760	62·3	152	67·30	82·44	105·64	131·90	1·185	1·451	1·859	2·321
1·765	62·5	153	67·76	83·01	106·31	132·80	1·196	1·465	1·877	2·344
1·770	62·8	154	68·17	83·51	106·91	133·61	1·207	1·478	1·894	2·365
1·775	63·0	155	68·60	84·02	107·62	134·43	1·218	1·491	1·911	2·386
1·780	63·2	156	68·98	84·50	108·27	135·20	1·228	1·504	1·928	2·407
1·785	63·5	157	69·47	85·10	109·05	136·16	1·240	1·519	1·947	2·432
1·790	63·7	158	69·96	85·70	109·82	137·14	1·252	1·534	1·965	2·455
1·795	64·0	159	70·45	86·30	110·58	138·08	1·265	1·549	1·983	2·479
1·800	64·2	160	70·96	86·92	111·32	139·06	1·277	1·565	2·003	2·503
1·805	64·4	161	71·50	87·60	112·25	140·16	1·291	1·581	2·026	2·530
1·810	64·6	162	72·08	88·30	113·15	141·28	1·305	1·598	2·048	2·558
1·815	64·8	163	72·96	89·16	114·21	142·65	1·322	1·618	2·074	2·589

Specific Gravity of Sulphuric Acid Solutions—*Continued.*

Sp. Gr. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 parts by weight of chemically pure Acid contain per cent.				1 Litre of chemically pure Acid contains kilograms of			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·820	65·0	164	73·51	90·05	115·33	144·08	1·338	1·639	2·099	2·622
1·821	...	...	73·63	90·20	115·59	144·32	1·341	1·643	2·104	2·628
1·822	65·1	...	73·80	90·40	115·84	144·64	1·345	1·647	2·110	2·635
1·823	...	...	73·96	90·60	116·10	144·96	1·348	1·651	2·116	2·643
1·824	65·2	...	74·12	90·80	116·35	145·28	1·352	1·656	2·122	2·650
1·825	...	165	74·29	91·00	116·61	145·60	1·356	1·661	2·128	2·657
1·826	65·3	...	74·49	91·25	116·93	146·00	1·360	1·666	2·135	2·666
1·827	...	...	74·69	91·50	117·25	146·40	1·364	1·671	2·142	2·675
1·828	65·4	...	74·86	91·70	117·51	146·72	1·368	1·676	2·148	2·682
1·829	...	...	75·03	91·90	117·76	147·04	1·372	1·681	2·154	2·689
1·830	...	166	75·19	92·10	118·02	147·36	1·376	1·685	2·159	2·696
1·831	65·5	...	75·46	92·43	118·41	147·88	1·382	1·692	2·169	2·708
1·832	...	...	75·69	92·70	118·73	148·32	1·386	1·698	2·176	2·717
1·833	65·6	...	75·89	92·97	119·07	148·73	1·391	1·704	2·184	2·727
1·834	...	...	76·12	93·25	119·43	149·18	1·396	1·710	2·191	2·736
1·835	65·7	167	76·38	93·56	119·84	149·70	1·402	1·717	2·200	2·747
1·836	...	...	76·57	93·90	120·19	150·08	1·406	1·722	2·207	2·755
1·837	...	...	76·90	94·25	120·71	150·72	1·412	1·730	2·217	2·769
1·838	65·8	...	77·23	94·60	121·22	151·36	1·419	1·739	2·228	2·782
1·839	...	...	77·55	95·00	121·74	152·00	1·426	1·748	2·239	2·795
1·840	65·9	168	78·04	95·60	122·51	152·96	1·436	1·759	2·254	2·814
1·8405	...	...	78·33	95·95	122·96	153·52	1·441	1·765	2·262	2·825
1·8410	...	...	78·69	96·38	123·45	154·20	1·448	1·774	2·273	2·838
1·8415	...	...	79·47	97·35	124·69	155·74	1·463	1·792	2·296	2·867
1·8410	...	...	80·16	98·20	125·84	157·12	1·476	1·808	2·317	2·893
1·8405	...	...	80·43	98·52	126·18	157·62	1·481	1·814	2·325	2·903
1·8400	...	...	80·59	98·72	126·44	157·94	1·483	1·816	2·327	2·906
1·8395	...	...	80·63	98·77	126·50	158·00	1·484	1·817	2·328	2·907
1·8390	...	...	80·93	99·12	126·99	158·60	1·488	1·823	2·336	2·917
1·8385	...	...	81·08	99·31	127·35	158·90	1·490	1·826	2·339	2·921

A table giving the relationship between the percentage content and the readings of the hydrometer employed in the United States has been published by Elliot.[1]

The tables calculated by Richmond[2] and by Marshall[3] from Pickering's measurements,[4] and which they regard as very exact, are not really so, since Pickering only employed a relative and not an absolute unit for his determinations; the figures consequently require to be corrected by multiplying by the factor 0·9974, as given by the German Standards Commission.[5]

Temperature Correction.

Since in practice specific gravity determinations are seldom made at exactly 15° C., it is necessary to have a means of correcting readings made at a higher or lower temperature.

[1] *J. Soc. Chem. Ind.*, 1898, **17**, 45.
[2] *Ibid.*, 1890, **9**, 479.
[3] *Ibid.*, 1899, **10**, 6.
[4] *J. Chem. Soc.*, 1890, **57**, 63 and 331.
[5] *Report*, 1904, p. 221.

Lunge has compiled a table, based on an extended series of observations, for this purpose. An abridged form of the complete table is given below.[1] A very complete table has also been published by the German Standards Commission, with which Lunge's table agrees very well down to a sp. gr. 1·100 = about 15 per cent. H_2SO_4. The table is inapplicable for weaker acids, owing to an error which cannot now be traced; it is however, seldom likely to be required for such weak acids.

Table showing the Influence of Temperature on the Specific Gravity of Sulphuric Acid.

a. Specific gravity at 15°/4°; under *t*, changes in specific gravity at the temperature *t*.

a.	*t.* 0°	*t.* 10°	*t.* 20°	*t.* 30°	*t.* 40°	*t.* 50°	*t.* 60°
1·840	+ 0·015	+ 0·005	− 0·005	− 0·015	− 0·025	− 0·034	− 0·044
1·820	16	5	5	16	26	37	47
1·800	17	5	5	16	27	37	47
1·780	17	5	5	16	27	37	47
1·760	16	5	5	16	26	36	47
1·740	16	5	5	15	25	35	45
1·720	15	5	5	15	25	35	44
1·700	15	5	5	14	24	33	43
1·680	15	5	5	14	24	33	42
1·660	14	5	5	14	23	32	41
1·640	14	5	4	14	23	32	40
1·620	14	4	4	14	22	31	40
1·600	14	4	4	13	22	31	39
1·580	14	4	4	13	22	30	39
1·560	13	4	4	13	21	30	38
1·540	13	4	4	13	21	30	38
1·520	13	4	4	13	21	29	37
1·500	13	4	4	12	21	29	37
1·480	13	4	4	12	20	28	36
1·460	12	4	4	12	20	28	36
1·440	12	4	4	12	20	28	35
1·420	12	4	4	12	19	27	35
1·400	12	4	4	12	19	27	34
1·380	12	4	4	11	19	27	34
1·360	11	4	4	11	19	26	34
1·340	11	4	4	11	19	26	33
1·320	11	3	4	11	18	26	33
1·300	11	3	3	11	18	26	33
1·280	11	3	3	11	18	25	33
1·260	11	3	3	11	18	25	32
1·240	11	3	3	10	18	24	32
1·220	10	3	3	10	17	24	31
1·200	10	3	3	10	17	23	30
1·180	10	3	3	10	16	23	29
1·160	9	3	3	9	15	22	28
1·140	8	3	3	8	14	20	27
1·120	8	2	2	8	14	19	25
1·100	7	2	2	7	13	18	24
1·080	6	2	2	7	12	17	23
1·060	5	2	2	6	10	16	21
1·040	3	1	1	5	9	14	20
1·020	2	1	1	4	8	13	18
1·010	2	1	1	4	7	12	17

[1] The complete table is given in *The Technical Chemist's Handbook*, Lunge, 2nd edition, 1916, pp. 126-129.

For temperatures below 15° the values given in the column *t* must, of course, be *subtracted* from the observed reading; for temperatures above 15° the corrections must be *added* to give the value at 15°. A table has also been calculated by Fuchs[1] for this correction.

The following table, p. 427, worked out by the *Chemische Fabrik*, Griesheim, will be found useful in many cases.

It is to be noted that the values given in all the above tables only hold good for chemically pure acid. In commercial acids the specific gravities at the highest concentrations are appreciably higher than the values given in the tables, but the variations between acids made at different works are too irregular to permit of a table being prepared for such acids. The specific gravity is influenced in the case of nitrous vitriol by the percentage of nitrous acid present, and in the case of chamber and concentrated acids by the presence of sulphurous acid, lead sulphate, nitrogen oxides, arsenic, and iron. The quantities of these usually present in sulphuric acid are too slight markedly to affect the specific gravity; but occasionally the acid is strongly contaminated with iron, aluminium, or sodium salts. The iron may result, for example, from pyrites dust, the aluminium from the packing of the Glover tower, or from the fireclay frequently employed for temporarily repairing leaks, the sodium salts from solutions of Chili saltpetre or Glauber's salts, which sometimes get into the chambers through carelessness. Nitric acid, which occurs in appreciable quantity in sulphuric acid recovered from spent nitrating acids, also causes an increase in the specific gravity.

The influence of impurities on the specific gravity of sulphuric acid has been dealt with by Lunge,[2] also in a paper by Marshall,[3] and in special detail by the German Standards Commission.[4] According to the Commission the Glover acid, as might be expected, is the most impure, the differences between the actual percentages found by analysis and those obtained by calculation from the tables varying from 0·5 to 1·87 per cent. "Commercially pure" chamber acid showed differences of 0·01 to 0·26 per cent.; acids of 142° Tw., of (exceptionally) 0·03 to 1·55 per cent.; acids of 168° Tw. made from chamber acid, differences of 0·24 to 0·76 per cent., in one instance only 0·02 per cent.; whilst acid free from arsenic differed from the actual percentage by from 0·09 to 0·65 per cent. Acids made by the contact process showed differences of only 0·02 to 0·23 per cent., and acid manufactured from sulphuretted hydrogen of only 0·02 to 0·18 per cent.

Since the changes in specific gravity with strength are very slight in the case of high-strength acids, and as it is just in these acids

[1] *Z. angew. Chem.*, 1898, **11**, 950.

[2] W. Wyld, *Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, 1923, p. 207.

[3] *J. Soc. Chem. Ind.*, 1902, **21**, 1503.

[4] *Report*, 1904, **5**, p. 243 *et seq.*

Reduction of the Hydrometer Readings for Sulphuric Acid between 65° and 66° B. (164° and 168° Tw.) to 15° C.

The hydrometer reading is taken from the first vertical column, and the observed temperature from the top line. The reading which lies vertically below the observed temperature and on the line containing the observed specific gravity gives the specific gravity at 15°.

°B.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
65·00	64·80	64·84	64·88	64·92	64·96	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60
65·10	64·90	64·94	64·98	65·02	65·06	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65.62	65·66	65·70
65·20	65·00	65·04	65·08	65·12	65·16	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80
65·30	65·10	65·14	65·18	65·22	65·26	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90
65·40	65·20	65·24	65·28	65·32	65·36	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00
65·50	65·30	65·34	65·38	65·42	65·46	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10
65·60	65·40	65·44	65·48	65·52	65·56	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20
65·70	65·50	65·54	65·58	65·62	65·66	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30
65·80	65·60	65·64	65·68	65·72	65·76	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40
65·90	65·70	65·74	65·78	65·82	65·86	65·90	65·94	65·98	66·02	66·06	66·10	66·14	66·18	66·22	66·26	66·30	66·34	66·38	66·42	66·46	66·50
66·00	65·80	65·84	65·88	65·92	65·96	66·00	66·04	66·08	66·12	66·16	66·20	66·24	66·28	66·32	66·36	66·40	66·44	66·48	66·52	66·56	66·60

that the impurities, always present in commercial acids, have the greatest effect on the specific gravity, which is increased by their presence, the tables for acids of over 90 per cent. strength should be used only for guidance in the works; for selling purposes, actual analyses should always be made.

Richmond and Merreywether[1] utilise the heat of admixture with water as a convenient and rapid means of ascertaining the strength of a sample of sulphuric acid. Into a Dewar vessel is put 400 g. of water, at a temperature near 18° C., which is measured by a thermometer reading to 0·01° C. When the temperature is constant, 5 c.c. of the strong acid is accurately run in from a pipette, and the acid is stirred by the thermometer till constancy is again reached. Then, from Pickering's results[2]

$$\text{Percentage of } H_2SO_4 = 100 - 7.335 \times \frac{400 + w}{400}\left(4.139 \times \frac{400}{400 + w} - R\right)$$

where w is the water equivalent of the calorimeter, and R is the rise of temperature.

Lichty[3] finds that pure monohydrate has a maximum freezing point, 10·43°–10·45° C., and a sharply marked minimum electrical conductivity of 0·01041 reciprocal ohm. For acids containing between 95 and 100 per cent. of monohydrate, measurement of the conductivity affords the most accurate means of determining their strength.

Boiling Points of Sulphuric Acid. Lunge.[4]

Per cent. H_2SO_4.	Specific Gravity.	Degrees Baumé.	Boiling Point. °C.	Per cent. H_2SO_4.	Specific Gravity.	Degrees Baumé.	Boiling Point. °C.	Per cent. H_2SO_4.	Specific Gravity.	Degrees Baumé.	Boiling Point. °C.
5	1·031	4·2	101	56	1·459	45·4	133	82	1·758	62·2	218·5
10	1·069	9·2	102	60	1·503	48·3	141·5	84	1·773	63·0	227
15	1·107	13·9	103·5	62·5	1·530	50·0	147	86	1·791	63·8	238·5
20	1·147	18·5	105	65	1·557	51·6	153·5	88	1·807	64·4	251·5
25	1·184	22·4	106·5	67·5	1·585	53·3	161	90	1·818	65·0	262·5
30	1·224	26·4	108	70	1·615	55·0	170	91	1·824	65·3	268
35	1·265	30·2	110	72	1·639	56·3	174·5	92	1·830	65·45	274·5
40	1·307	33·9	114	74	1·661	57·4	180·5	93	1·834	65·65	281·5
45	1·352	37·6	118·5	76	1·688	58·8	189	94	1·837	65·8	288·5
50	1·399	41·1	124	78	1·710	60·0	199	95	1·840	65·9	295
53	1·428	43·3	128·5	80	1·733	61·0	207	...	...	...	...

[1] *Analyst*, 1917, **42**, 273.
[2] *J. Chem. Soc.*, 1890, **57**, 94.
[3] *J. Amer. Chem. Soc.*, 1908, **30**, 1834.
[4] *Ber.*, 1878, **11**, 370.

Melting Points of Sulphuric Acid. Knietsch.[1]

Enlarged by Lunge by the addition of the corresponding percentage of H_2SO_4.

The melting points given in the table are the temperatures which remain constant during the period of complete crystallisation ; that is, from the temperature at which crystals begin to appear in the cooled acid until the stage when the mass becomes solid after removal from the freezing mixture.

Sulphuric Acid.								
Total SO_3 per cent.	H_2SO_4 per cent.	Melting Point. °C.	Total SO_3 per cent.	H_2SO_4 per cent.	Melting Point. °C.	Total SO_3 per cent.	H_2SO_4 per cent.	Melting Point. °C.
1	1·22	− 0·6	23	28·17	−40·1	80	98·00	+ 3·0
2	2·45	− 1·0			Under	81	99·25	+ 7·0
3	3·67	− 1·7	...	...	−40·0	81·63	100·00	+10·0
4	4·90	2·0	61	74·72	−40·0	82	...	+ 8·2
5	6·12	− 2·7	62	75·95	−20·0	83	...	− 0·8
6	7·35	− 3·6	63	77·17	−11·5	84	...	− 9·2
7	8·57	− 4·4	64	78·40	− 4·8	85	...	−11·0
8	9·80	− 5·3	65	79·62	− 4·2	86	...	− 2·2
9	11·02	− 6·0	66	80·85	+ 1·2	87	...	+13·5
10	12·25	− 6·7	67	82·07	+ 8·0	88	...	+26·0
11	13·47	− 7·2	68	83·39	+ 8·0	89	...	+34·2
12	14·70	− 7·9	69	84·52	+ 7·0	90	...	+34·2
13	15·92	− 8·2	70	85·75	+ 4·0	91	...	+25·8
14	17·15	− 9·0	71	86·97	− 1·0	92	...	+14·2
15	18·37	− 9·3	72	88·20	− 7·2	93	...	+ 0·8
16	19·60	− 9·8	73	89·42	−16·2	94	...	+ 4·5
17	20·82	−11·4	74	90·65	−25·0	95	...	+14·8
18	22·05	−13·2	75	91·87	−34·0	96	...	+20·3
19	23·27	−15·2	76*	93·10	−32·0	97	...	+29·2
20	24·50	−17·1	77*	94·83	−28·2	98	...	+33·8
21	25·72	−22·5	78*	95·05	−16·5	99	...	+36·0
22	26·95	−31·0	79	96·77	− 5·2	100	...	+40·0

* So-called 168° Tw.

Qualitative Examination of Sulphuric Acid for Impurities

The impurities likely to be present in ordinary commercial sulphuric acid are :—Sulphates of sodium (less frequently potassium), ammonium, calcium, aluminium, iron and lead, exceptionally also of zinc and copper ; arsenic, selenium, thallium, titanium, nitrogen oxides, hydrochloric acid, sulphurous acid, and hydrofluoric acid.

Acidum sulfuricum purissimum is, according to Krauch,[1] tested for fixed residue, nitric acid, selenium, reducing substances, lead, other metals, arsenic, ammonia, and the halogens.

General examination for gaseous impurities (Warington). Two kilos of the undiluted acid are thoroughly shaken in a flask, of a capacity equal to twice the volume of the acid, so as to saturate the

[1] *Ber.*, 1901, 34, 4100.

[2] *The Testing of Chemical Reagents for Purity* (1919), p. 322.

air in the flask with the gases dissolved in the acid. The atmosphere in the flask is then tested for sulphurous acid by iodised starch paper and for gaseous oxides of nitrogen by potassium iodide starch paper. Any blue coloration produced by the latter gases will not be destroyed by sulphurous acid unless this is present in considerable excess. Sulphuretted hydrogen reacts like sulphurous acid in this test.

Sulphurous acid. This gas will decolorise a starch solution rendered faintly blue by iodine; or it may be converted into sulphuretted hydrogen by means of zinc or aluminium, and examined by lead acetate paper or by an alkaline solution of sodium nitroprusside. The latter is a very delicate test.

Hydrochloric acid. Two g. are diluted to 30 c.c., and a few drops of silver nitrate solution added; in the case of acid. sulfuric. puriss. no turbidity should result. The hydrochloric acid present in ordinary commercial vitriol arises from the sodium chloride present in the nitre.

The qualitative examination for traces of nitrogen acids is best made with diphenylamine. The diphenylamine is dissolved in about 100 parts of pure sulphuric acid, or failing this, in an acid freed from nitrogen compounds by boiling with the addition of a very small amount of ammonium sulphate, and the solution diluted with about $\frac{1}{10}$ of its volume of water. The solution may be used at once, or may be kept some time; but it gradually becomes discoloured and less sensitive. In testing concentrated sulphuric acid for nitrogen acids about 2 c.c. of the acid is placed in a test-tube or conical test-glass, and about 1 c.c. of the diphenylamine solution added carefully so that the two layers only mix slowly; in the case of weaker acids or other solutions of lower specific gravity the order is reversed, and the heavier diphenylamine solution placed below. The slightest trace of nitrogen acids is shown by the development of a beautiful blue colour at the junction of the two solutions.[1]

In the presence of *selenium* (for the detection of which see *infra*), which also gives the above reaction with diphenylamine, nitrogen acids, if present in somewhat large quantity, may be recognised by the decolorising effect on indigo solution, whilst if only present in traces they may be detected by the reddening produced in a solution of brucine sulphate. The detection of nitrogen acids by means of ferrous sulphate has been described above (p. 411).

Nitrous acid can be detected by a number of very delicate reactions, which are not given by nitric acid. These include the blue coloration produced in potassium iodide starch solution, or still better in zinc iodide starch solution. Its presence is detected with especial ease by the formation of azo-colours, a reaction first discovered by Griess,

[1] *Cf.* Lunge, *Z. angew. Chem.*, 1894, 7, 345.

who recommended the use of metaphenylenediamine, which gives rise to a yellow coloration, and also the still more sensitive reaction with sulphanilic acid and α-naphthylamine, which produces a rose coloration. The latter reagent has the disadvantage that the naphthylamine solution, even when prepared from a perfectly white salt, becomes dark coloured after a relatively short time, and as a result loses its sensitiveness. Further, in very dilute solutions, such as 1 in 1000 millions, the reaction takes place so slowly that it is impossible to be quite certain that the coloration arises from the substance tested and not from nitrous acid present in the air; the time may be appreciably shortened by warming the solution, but even in this case fifteen to twenty minutes may be necessary.

Ilosvay[1] found that by using acetic acid instead of sulphuric acid or hydrochloric acid, the time required for the reaction is very much decreased, and that at the same time the colour is developed to a much greater extent. He overcomes the difficulty of the discoloration of the naphthylamine by adopting the following method of preparing the solution:—0·5 g. of sulphanilic acid is dissolved in 150 c.c. of dilute acetic acid and 0·1 g. of solid naphthylamine is boiled with 20 c.c. of water, the colourless solution poured off from the bluish-violet residue, and 150 c.c. of dilute acetic acid added to this solution. In testing, a few c.c. of the sulphanilic acid solution are added to about 20 c.c. of the solution to be examined, the mixture warmed to 70° to 80°, and the naphthylamine solution then added. In the presence of one part of nitrous acid in 1000 million parts of solution the red coloration, due to the azo-colour produced, appears in about a minute; if the nitrous acid be present in relatively large amount, about 1 : 1000, only a yellow solution is obtained unless a concentrated solution of naphthylamine be employed.

Lunge[2] mixes the solutions of sulphanilic acid and naphthylamine prepared according to Ilosvay's directions, and keeps the mixture in a well-stoppered bottle. It is unnecessary to exclude light from the mixed solutions, but it is essential to prevent access of air, since this may possibly contain nitrous acid as an impurity. By thus combining the two reagents in a single solution, any contamination by nitrous acid from the atmosphere is at once evidenced by the red colour of the solution. A solution that has become red may be very quickly rendered fit for use by shaking with zinc dust and filtering. With the reagents ready mixed, the reaction may also be hastened by warming the solution to 70° to 80°. (Cf. *infra*, under the quantitative application of the method.)

Riegler[3] recommends the use of naphthionic acid or sodium

[1] *Bull. Soc. Chim.*, 1889 [3], **2**, 317.
[2] *Z. angew. Chem.*, 1889, **2**, 666.
[3] *Z. anal. Chem.*, 1896, **35**, 677; 1897, **36**, 306, 377, 665.

naphthionate and β-naphthol, but this has no advantage over Griess' reagents, and according to Riegler himself is not so sensitive (1 : 100 million). This reagent can be used colorimetrically.

For other methods see H. Erdmann [1] and Mennicke.[2]

Brucine in sulphuric acid solution reacts only with nitric acid and not with nitrous acid when sulphuric acid is present in large excess; nitrous acid only gives a coloration if the solution contains at least two parts of water to each part of sulphuric acid. Consequently, to test only for nitric acid, the solution should contain sulphuric acid equal to 2/3 of its volume, and the test be carried out by adding 1 c.c. of a solution of 0·2 g. brucine in 100 c.c. strong sulphuric acid, to 50 c.c. of the solution to be examined. In the presence of 0·01 mg. nitrate-nitrogen, a red colour results, subsequently passing through orange to a golden yellow.[3]

Hydrofluoric acid may be detected by warming the acid in a platinum dish, covered with a glass plate coated with wax in which figures have been scratched.

Ammonia. Two g. of the acid is diluted with about 30 c.c. of water, the solution made alkaline by the addition of a potassium hydroxide solution containing 3 to 4 g. pure hydroxide, and ten to fifteen drops of Nessler's reagent added; no distinctly yellow or brownish-red coloration should result.

Krauch states that by this method 1 mg. NH_3 in 100 g. concentrated sulphuric acid will produce a distinct yellow coloration and turbidity.

Solid impurities. Lead is shown by any turbidity which results on the addition of five volumes of strong alcohol to one volume of the acid; simple dilution with water is sufficient if the lead be present in considerable quantity.

Iron. The acid is boiled, after the addition of one drop of pure nitric acid, diluted slightly, and when cold, treated with an excess of thiocyanate solution. A blank test should always be made with the nitric acid employed, to make sure that any red coloration produced is not due to this.

Venable[4] employs a mixture of cobalt nitrate and strong hydrochloric acid. Traces of ferric salts change the blue colour of the solution to green; ferrous salts do not affect it.

Selenium is recognised by the red coloration and subsequent red precipitate produced by the addition of ferrous sulphate, or, preferably, sulphurous acid to the solution; the reaction is hastened by warming. The presence of 0·01 per cent. of selenium is shown, after some hours, by either reagent. Selenic acid cannot be tested for by these reagents,

[1] *Z. angew. Chem.*, 1900, 13, 33. [2] *Ibid.*, 1900, 13, 235 and 711.
[3] *Cf.* Winkler, *Z. angew. Chem.*, 1901, 14, 170; and, Lunge, *ibid.*, 1901, 14, 241.
[4] *Z. anal. Chem.*, 1889, 28, 699.

but it may be detected by means of acetylene, which also reacts with selenious acid, and produces a red coloration in the presence of only 0·001 per cent. of selenium; a little hydrochloric acid hastens the separation of the selenium, which is soluble in hot sulphuric acid, forming a green solution.

Detection and Approximate Estimation of Arsenic

Examination for this impurity is always important, and it is necessary in all cases where the acid is sold as pure, or is intended for use in the preparation of substances such as glucose, tartaric acid, mineral water, yeast, etc., which either directly or indirectly may be used as food-stuffs. Sulphuric acid prepared from pyrites, unless specially purified, usually contains from 0·1 to 0·2 per cent. of arsenious oxide, and, in exceptional cases, up to 1 per cent. and more.

Very special attention has been directed to the presence of arsenic in sulphuric acid, owing to the numerous and in some instances fatal cases of arsenical poisoning that occurred in the year 1900. It was found that these cases arose from the consumption of beer, in the brewing of which glucose containing arsenic had been employed, the arsenic in the glucose being traced in turn to the sulphuric acid used in its manufacture. The investigation into the origin of this poisoning led to the publication of much important work on the detection and estimation of arsenic in various materials.[1]

Of the various methods of testing for arsenic, that of Marsh, more recently and correctly known as the Marsh-Berzelius test, is by far the most generally employed; the Reinsch and the Gutzeit methods are also largely used.

As a sequel to the outbreak of arsenical poisoning referred to above, a joint committee of the Society of Chemical Industry and of the Society of Public Analysts was appointed in 1901 to investigate the various methods for the detection and approximate estimation of arsenic in beer, brewers' materials, food-stuffs, and fuels;[2] this committee reported in favour of the Marsh-Berzelius test as the most reliable and generally applicable method.

According to Hehner,[3] ordinary pyrites vitriol contains on the average 0·2 per cent. of arsenious acid (As_2O_3); such acid, after purification, he considers permissible for use in the preparation of foods and for the other purposes mentioned above, provided that the arsenic left in does not exceed 0·05 mg. As_2O_3 in 10 g. of the acid, that is, one part As_2O_3 in

1 *Cf.* Report of the Royal Commission on Arsenical Poisoning, 1903; *J. Soc. Chem. Ind.*, 1904, **23**, 159.

2 The full Report of the Committee is published in the *J. Soc. Chem. Ind.*, 1902, **21**, 94.

3 *J. Soc. Chem. Ind.*, 1901, **20**, 188.

200,000 parts of acid. Very frequently the amount of arsenic remaining after purification is less than this limiting value, but no acid prepared from pyrites, and perhaps not even that from Sicilian brimstone, is absolutely free from arsenic; on the other hand, such freedom might be expected in acid made by the contact process when platinum is employed as the contact material. Acid prepared by the ferric oxide contact process is not free from arsenic (Conroy).

A. The Marsh-Berzelius Test.

The actual test, as proposed by Marsh in 1827, consisted in the formation of a dark stain on a piece of cold porcelain brought into a burning mixture of hydrogen and arseniuretted hydrogen. For more exact purposes, this is generally combined with the Berzelius reaction by heating the arsenical hydrogen during its passage through a glass tube, and so decomposing the arseniuretted hydrogen with the separation of the arsenic in the form of a mirror.

The following are the details and conditions for carrying out the test as recommended by the joint committee of the Society of Chemical Industry and the Society of Public Analysts.

The materials required are:—

1. *Hydrochloric acid.* The purest hydrochloric acid obtainable is very rarely free from arsenic. To the "pure" acid as purchased for analysis diluted with distilled water to a sp. gr. of 1·10, sufficient bromine is added to colour it strongly yellow (about 5 c.c. per litre); sulphurous acid, either gaseous or in aqueous solution, is then added *in excess*, and the mixture allowed to stand for at least twelve hours; or hydrobromic acid and sulphurous acid may be used. The acid is then boiled till about one-fifth has evaporated, and the residue can either be used direct or it may be distilled; the whole of the arsenic is volatilised with the first portion.

2. *Sulphuric acid.* This is more frequently obtainable arsenic-free than hydrochloric acid. If not procurable, to about half a litre of sulphuric acid, "pure for analysis," a few grams of sodium chloride are added and the mixture distilled from a non-tubulated glass retort, the first portion of the distillate, about 50 c.c. being rejected. For the purpose of the test, one volume of the distilled acid is diluted with four volumes of water.

3. *Nitric acid* can, as a rule, be obtained free from arsenic, without much difficulty, the pure redistilled acid being used. This should be tested by evaporating 20 c.c. in a porcelain dish, which should then be washed out with dilute acid, and tested as described below.

The purified acids should be prepared as required, and should not be stored for any length of time. If they must be stored, however,

Jena flasks are to be preferred, since most bottle glass is liable to communicate traces of arsenic.

4. *Zinc.* Arsenic-free zinc is obtainable from chemical dealers It should be re-granulated by melting and pouring it from some height into cold water. A. H. Allen holds it to be essential, both for a regular evolution of hydrogen and for the formation of uniformly deposited brown-coloured mirrors, that the zinc should contain a trace of iron.

5. *Calcium hydroxide.* Even when made from white marble this

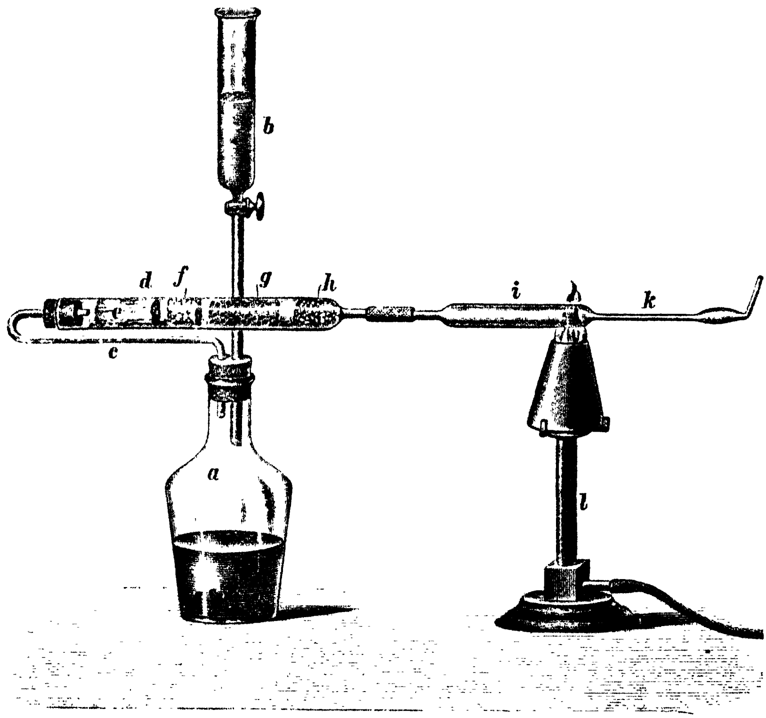

FIG. 194.

is not always free from arsenic; a selection must, therefore, be made from various samples. If pure lime is not obtainable, magnesia may equally well be used, and can more readily be obtained of sufficient purity.

6. *Calcium chloride.* This salt often contains arsenic, and before being used as a drying agent must be freed from the volatilisable part of the impurity by moistening it with strong hydrochloric acid, fusing, and re-granulating.

The apparatus to be used is shown in Fig. 194.

A bottle or flask, *a* (which for frothing materials should preferably be wider at the top than at the bottom), holding about 200 c.c.. is fitted

with a doubly bored cork or rubber stopper, or with a ground-in glass connection carrying a tap funnel, *b*, holding about 50 c.c., and an exit tube, *c*. The latter is connected with a drying tube, *d*, containing first a roll of blotting-paper, *e*, soaked in lead acetate solution and dried, or a layer of cotton wool prepared in a similar way, then a wad of cotton wool, *f*, then a layer, *g*, of granulated calcium chloride, and finally a thick wad, *h*, of cotton wool. To this tube is fitted a hard glass tube, *i*, drawn out as shown in the figure to a thinner tube, *k*, and of such external diameter that at the place where the arsenic mirror is to be expected, the tube just passes through a No. 13 Birmingham wire gauge (corresponding with 0.092 inch = 2·34 mm.). The exact size is not material, but all tubes used for standards and tests should be as nearly as practicable of the same diameter. A good Bunsen flame is used to heat the hard glass tube close to the constriction. About one inch of tube, including the shoulder, ought to be red hot. A piece of moderately fine copper gauze, about one inch square, wrapped round the portion of the tube to be heated, assists in ensuring an equal distribution of heat.

Method of testing. About 20 g. of zinc is placed in the bottle, *a*, and washed with water to clean the surface, as particles of dust may contain arsenic; all the parts of the apparatus are connected up, and a quantity of acid, prepared as described, is allowed to flow from the funnel, *b*, so as to cause a fairly brisk evolution of hydrogen. When the hydrogen flame, which during the heating of the tube, *i*, should be kept at as uniform a height as possible (about a quarter of an inch), burns with a round, not pointed tip, all air has been removed from the apparatus. The plug in *d* prevents the flame from striking back. The burner is then placed under the hard glass tube as described, and more acid (10 to 20 c.c. is generally enough) run in as required. With good materials no trace of a mirror is obtained within half an hour. Great care must be taken that when additions of acid are made to the zinc, no air-bubbles are introduced, since in presence of air the arsenic mirror may become black and unevenly distributed; when the experiment is properly conducted the mirror is brown. Should the blank experiment not be satisfactory, it must be ascertained, by changing the materials methodically, whether the fault lies with the acid, zinc, or other materials, or with the apparatus.

Preparation of standard mirrors. When a satisfactory blank experiment has been obtained, a series of standard mirrors are prepared under the following conditions:—

A hydrochloric acid solution of arsenious oxide, containing 0·001 mg. As_2O_3 per c.c., is prepared by diluting a stronger solution with distilled water. Two c.c. of this solution, equal to 0·002 mg. of arsenious oxide, is introduced into the apparatus, a new tube, *ik*, having been joined to the drying tube. If the zinc is sensitive, a distinct brown mirror is

obtained after twenty minutes. It is important to note that some "pure" zinc is, from a cause at present unknown, not sufficiently sensitive; that is to say, the addition of minute quantities of arsenic produces no mirror (on this point see p. 412). The portion of the tube, *ik*, containing the mirror is sealed off while still filled with hydrogen; in contact with air the mirrors gradually fade. Mirrors are then similarly made with 0·004, 0·006, 0·008, and 0·01 mg. of arsenious oxide. With a little practice it is easy to obtain the deposits of arsenic neatly and equally distributed. The standard mirrors, properly marked, are mounted on a white card or porcelain slip. It is important to bear in mind that the first stage of every test must be a blank of at least twenty minutes.

Hydrochloric acid is somewhat more sensitive than sulphuric acid; that is to say, it gives rather denser mirrors with minute quantities of arsenic. If for any reason sulphuric acid is preferred, the set of standard mirrors must be prepared with this acid.

Organic materials, such as beer, yeast, etc., cannot be tested, when sulphuric acid is used, without destruction of the organic matter, whilst, as a rule, they can be directly tested with hydrochloric acid. However, many materials are met with in which it is preferable to destroy the organic matter.

Procedure without destruction of organic matter. The apparatus is started and a blank experiment allowed to go on for twenty minutes. If no trace of a deposit is obtained, 10 c.c. of the liquid to be tested, and 10 c.c. of hydrochloric acid are put into the funnel, *b*, and slowly introduced into the bottle, care being taken to exclude air-bubbles. Some materials, such as beers, are apt to froth, hence the necessity for the slow introduction of the sample. If after about ten minutes no mirror appears, another 10 c.c. of the liquid with 10 c.c. of hydrochloric acid are added, and the experiment continued for from fifteen to twenty minutes, acid being added from time to time as may appear necessary.

The report also deals with the special precautions to be observed in the examination of malt, hops, sugar, and other brewing materials, as well as the particulars for cases in which the organic matter present must be destroyed, as is frequently essential. Fuel, for example, is incinerated after mixing with lime or magnesia, and the resulting residue extracted with hydrochloric acid to obtain the "total arsenic."

If sulphites are present they must be oxidised by bromine, the excess of the latter being removed by heating.

The committee found that arsenic acid as well as arsenious acid can be detected and estimated by the procedure described. The quantitative results are, of course, only approximate, and cannot be relied upon for quantities of arsenious oxide below 0·003 mg. As an additional precaution, a second tube should always be substituted for that containing the mirror, and the experiment continued for a further period of

from fifteen to twenty-five minutes, and any arsenic deposited added to that previously obtained. As a further check, the tests should always be made in duplicate.

To prove that the mirror obtained actually consists of arsenic, the narrow portion of the tube, which should not contain more arsenic than corresponds to 0·01 mg. As_2O_3, is cut off, the hydrogen displaced by air, and the ends of the tube then fused together. The sealed-up tube is then drawn several times through a Bunsen flame until the mirror has disappeared; on cooling, minute crystals of arsenious oxide appear. The sparkling of the crystals can be seen with the naked eye, if the tube be held in front of a luminous flame, and the crystals may be readily identified under the microscope.

By carrying out the test in the manner described, it is possible to detect, when working with 20 g. or 20 c.c. of substance, as low a percentage as 0·000015 As_2O_3 or one part As_2O_3 in 7,000,000.

The foregoing description is intended for the detection of extremely minute quantities of arsenic in food-stuffs and the like for forensic purposes; fuel is included on account of its use in the "kilning" of malt.

For the examination of sulphuric acid the method may be simplified by suitable modifications. For works purposes, for example, in testing whether, in purifying, all the arsenic has been precipitated by sulphuretted hydrogen, a much simpler apparatus will suffice, the test being frequently carried out in a flask fitted with a glass tube drawn out to a point and bent at right angles, and the examination made by observing whether the hydrogen flame will produce a stain on cold porcelain. If no stain is produced, it is assumed that only harmless traces of arsenic remain in the acid.

A further refinement in the method for the detection of arsenic has resulted from the work of the special Committee,[1] appointed by the Board of Inland Revenue, of which Prof. T. E. Thorpe acted as chairman. In the report two methods of carrying out the Marsh-Berzelius test are described, namely, the zinc method and the electrolytic method. The details for the first agree with those of the earlier arsenic committee (p. 434), except that the apparatus recommended is much smaller and the quantities of acid and zinc employed correspondingly less. The gas evolution takes place more slowly and the arsenic is deposited on a smaller surface of glass, which latter allows of a better comparison with the standard mirrors. These improvements are considered essential by the Inland Revenue Committee. Where cost of apparatus need not

[1] Report of the Committee appointed by the Commissioners of Inland Revenue to specify the ingredients of beers and the materials used in their preparation which are liable to be contaminated by arsenic, and to prescribe tests, etc.; published by Wyman & Sons, London, 1903. *Cf.* also, *J. Chem. Soc.*, 1903, 83, 974.

be considered and where suitable electrical current is available, the evolution of hydrogen by electrolysis is recommended. The design of the apparatus and the manner of carrying out the test, as worked out in the Government Laboratory, are illustrated and minutely described in the report. In this method the conditions of experiment may be made absolutely uniform, and more exact comparisons with the standard mirrors should, in consequence, be obtained; further, all troubles arising from the presence of arsenic in the zinc are eliminated.

The apparatus, Fig. 195, consists of the following parts. The glass vessel A, open below, is fitted with a ground-in stopper furnished with a tap funnel the tube of which projects slightly below the stopper. The

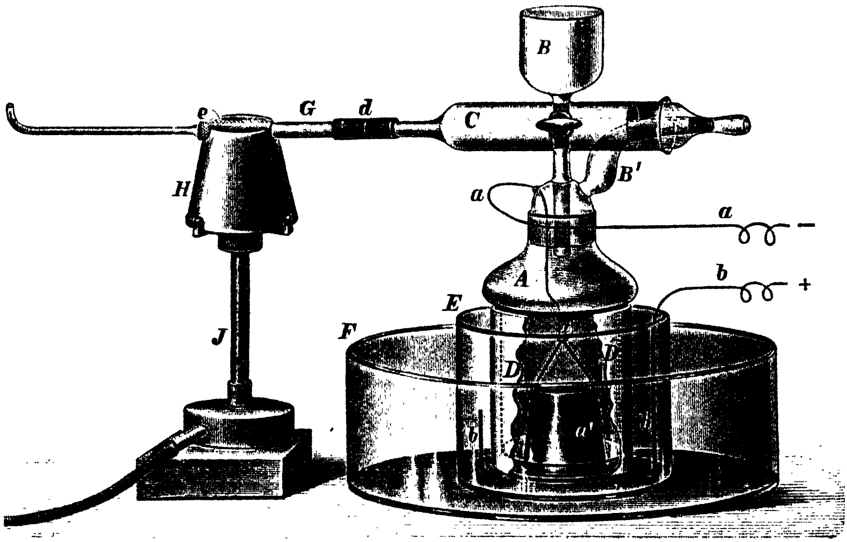

FIG. 195.

stopper is provided with a bent tube B', to which the calcium chloride tube C is attached by a ground-glass connection. A strong platinum wire, *a*, is also fused into the stopper, and to it a conical-shaped platinum cathode, *a'*, pierced with several holes, is attached. The vessel A is supported by a porous cell D, the distance between the walls of the two vessels being from 2 to 3 mm. The porous cell is made of Pukall's porous porcelain, the walls of which are from 1 to 1·5 mm. thick; it stands in the thick-walled, glass anode vessel E. The anode consists of a strip of platinum foil, 2 cm. broad, coiled loosely round the cell D, and connected to the circuit by a strong platinum wire. The whole stands in a cooling-vessel, F, by aid of which the temperature is kept below 50°. The tube C contains firstly a plug of cotton wool, then for a length of 5 cm. pure, rather finely granulated, calcium chloride, which must be renewed after every three or four experiments, followed by a second

plug of cotton wool, and finally a roll of lead acetate paper; this is prepared by soaking filter paper in a cold saturated solution of lead acetate, and after drying in the air, cutting it into strips 1 cm. wide and then rolling it into a coil so as to fit loosely in the tube. A further small spiral roll of lead paper is also inserted in the exit-tube from C, which is connected with the constricted glass tube G by means of a small piece of non-vulcanised rubber, care being taken that the ends of the glass tubes are in contact. The tube G is made from a piece of Jena glass tubing of 3·5 mm. internal and 5 mm. external diameter, and is cleaned by successive treatment with acid, alcohol, and water. It is then dried and heated in the blowpipe so that a portion of the tube, about 2 cm. in length and 5 cm. from the end, is softened, when it is drawn out to a length of 7 to 8 cm. and to a uniform external diameter of 2 mm. The tube is then cut off near the end of the narrowed portion and the latter bent upwards to a height of 1 cm.; it is supported in slots in the metal cone H, surrounding the Bunsen flame; a piece of platinum gauze, *c*, about 2 cm. square, is wrapped round the portion of the tube to be heated in the burner. The small burner J has a circular base 12 mm. high and a tube 6 cm. high, and 5 mm. internal diameter.

The resistance of the apparatus is 1·4 ohms, and working at 7 volts potential difference between the pole wires and employing a current of 5 amperes, 40 c.c. of hydrogen are liberated per minute; this gives a steady flame 2 mm. high. The original description contains directions for arranging the apparatus so as to permit several tests being carried out simultaneously.

The sulphuric acid solution employed in the apparatus is prepared from pure sulphuric acid, tested especially for freedom from arsenic, which is diluted in the proportion of 1 vol. of concentrated acid to 7 vols. of water.

To apply the test to sulphuric acid, 5 c.c. of the sample is diluted with 20 c.c. of water, 0·5 g. potassium metabisulphite added, the solution boiled to drive off the sulphur dioxide, and allowed to cool. The object of the addition of the metabisulphite is to reduce any arsenic acid or arsenate present to the arsenious state, as this electrolytic method is only applicable to arsenic in the condition of an arsenite or of arsenious acid.

To carry out a test, the vessels A, B, and E are first thoroughly washed with water, cold water poured into the cooling vessel F, and the tube G connected with the drying tube C as described. The wires *a* and *b* are then connected with the current source by means of binding screws, 30 c.c. of dilute sulphuric acid poured into the anode vessel E, and 20 c.c. into the porous cell D through the funnel B; the current is then switched on; after ten minutes the air will have been sufficiently

displaced to allow the hydrogen to be lighted. At the same time the burner J is lighted, and the flame so adjusted that the platinum gauze *e* is maintained at a red heat. If at the end of a further fifteen minutes no brown ring has appeared in the narrow portion of the tube G, it is safe to assume that the acid is free from arsenic. If this be the case, 2 c.c. of rectified amyl alcohol is admitted to D through B, and followed immediately by the acid to be tested, which has previously been prepared as described above, and the funnel rinsed with 5 c.c. of water; the funnel tube is thus kept full of liquid, and air excluded from the apparatus. The object of the addition of the amyl alcohol is to prevent frothing. If arsenic be present, a deposit will be formed, after a few minutes, at a point 1 to 2 cm. removed from the heated portion of the tube; after thirty minutes practically all the arsenic will in most cases have been deposited. The tap in B is then opened, the outer end of G immediately held with a pair of forceps, and a small pointed flame directed against the tube between the end and the deposit at a point 3 cm. from the latter. The tube fuses together immediately and is drawn off. The electric current is then switched off and the tube G heated and drawn out near its wider end, care being taken not to heat the arsenic mirror. The piece of tube about 4 cm. long so obtained and containing the arsenic mirror, is placed on a piece of white paper and compared with standard mirrors prepared from very small quantities of arsenic employed in the form of a solution of pure arsenious acid in hydrochloric acid, and diluted so that 1 c.c. contains 0·01 mg. As_2O_3.

In order to obviate the necessity of reducing arsenic acid and arsenates, Trotman[1] adds a few drops of zinc sulphate solution to the contents of the inner cell; this causes the hydrogen to be evolved in a state of overvoltage which suffices to reduce any pentavalent arsenic present. The same object has been more satisfactorily attained by using cathodes of metals, such as lead and zinc, which have a considerably greater overvoltage than platinum. Sand and Hackford[2] recommend the use of lead electrodes, and have described a suitable apparatus for the electrolytic estimation of minute quantities of arsenic, whilst W. Thomson[3] recommends zinc electrodes; in both cases a complete reduction of the arsenic is said to be effected. Chapman and Law[4] have shown that arsenite solutions are completely reduced in presence of sulphuric acid when cathodes of lead, tin, or of cadmium are used, but that with other metals, including iron, a large proportion of the arsenic is retained in the cell; arsenate solutions behave similarly, but in no case is the whole of the arsenic evolved as hydride.

Kühn and Saeger[5] have described a modified form of the Marsh

[1] *J. Soc. Chem. Ind.*, 1904, **23**, 177.
[2] *J. Chem. Soc.*, 1904, **85**, 1018.
[3] *J. Soc. Chem. Ind.*, 1904, **23**, 799.
[4] *Analyst*, 1906, **31**, 3.
[5] *Ber.*, 1890, **23**, 1798.

test, which permits of a quantitative estimation of the arsenic. Ackroyd[1] states that only the brown and not the blue modification of the arsenic mirror is suitable for quantitative comparison; the former results in the case of organic liquids (glucose, beer, etc.), the latter from inorganic solutions. Only dilute solutions should be employed in testing, and for exact work fresh standards should be made each time.

Bertrand[2] has proposed the following method for the detection of $\frac{1}{1000}$ mg. arsenic or less. The acid used is warmed to from 30° to a maximum of 60°, the zinc added, and all air driven out of the apparatus by pure carbon dioxide; 1 to 2 drops of platinic chloride solution and 15 c.c. of dilute sulphuric acid (1 : 5) added, followed after an interval of ten minutes by the solution to be tested. The gas evolved is dried by passing through a plug of cotton wool previously heated to 120°, and then through a carefully cleaned glass tube of 1 mm. diameter, which is narrowed by drawing out at a point some 10 to 15 cm. behind the place at which the ring is to be produced. A length of 20 cm. of the tube is heated to incipient redness. In the case of thick-walled tubes it is advisable to confine the heated space by means of strips of filter paper which are kept moist. Finally, the tube is sealed at both ends in a current of hydrogen. According to Treadwell,[3] the addition of platinic chloride is inadmissible. Pederson[4] gives similar details to those of Bertrand.

The zinc sometimes appears to be quite inactive (*cf.* p. 437), but such zinc has the peculiar property of becoming active on remelting and granulating. Allen ascribes this to the trace of iron, which may be taken up on melting in an iron ladle, and on this account he purposely adds a trace of ferric sulphate. Large quantities of iron are, however, to be avoided, since according to Parsons and Stewart[5] they cause a portion of the arsenic to be retained in the hydrogen generating flask. The influence of metallic salts on the sensitiveness of zinc has been especially studied by Chapman and Law.[6] Salts of palladium, platinum, nickel, and of cobalt prevent the reduction of arsenic to its hydride by zinc, whilst those of cadmium, tin, lead, aluminium, magnesium, and the alkali metals have no effect. Alloys of most metals with "sensitive" zinc, similarly inhibit the reduction, with the exception of the alloys of zinc with tin and with cadmium. If, however, 2 g. of cadmium sulphate, or of stannous chloride, or of lead acetate, be added to one of these insensitive alloys (with the exception of that with nickel), the whole of the arsenic is evolved as hydride. Similarly, the addition of 2 g. of cadmium sulphate to the apparatus containing insensitive zinc renders it capable of reducing arsenic compounds;

[1] *J. Soc. Chem. Ind.*, 1902, **21**, 1900.
[2] *Bull. Soc. Chim.*, 1902 [3], **27**, 851.
[3] *Analytical Chemistry*, 4th edition, vol. i., p. 233.
[4] *Chem. Centr.*, 1903, I., 250.
[5] *J. Amer. Chem. Soc.*, 1902, **24**, 1005.
[6] *Analyst*, 1906, **31**, 3.

also, magnesium is rendered sensitive by the addition of a cadmium, zinc, or lead salt.

Arsenic-free zinc is readily prepared, according to Hehner,[1] by melting about 500 g. of zinc with about 1 g. of metallic sodium ; on stirring, a black scum is formed on the surface of the metal, which is removed. The fused metal is then poured into a second crucible, again treated with sodium, and granulated. If this treatment is carefully carried out, the zinc obtained is absolutely free from arsenic. Pattinson and Dunn found it preferable to distil the zinc from the zinc-sodium alloy.

The suggestion to employ aluminium foil and sodium hydroxide in place of zinc, cannot be recommended for exact work. According to Hehner,[2] it is possible, when working with aluminium and sodium hydroxide solution, to fail in obtaining a mirror even when 0·2 mg. of arsenious oxide is present in 25 c.c. of the solution.

Great differences of opinion exist as to the influence of sulphites, which are frequently present in beer. According to some authorities they interfere with the formation of the arsenic mirror, and should consequently be oxidised with bromine water before testing (*cf.* p. 437), whilst others maintain that they exert no prejudicial effect. The extremely small amount of sulphur dioxide which may be present in sulphuric acid need scarcely be considered. The presence of sulphites only calls for consideration in the examination of beer, to which calcium bisulphite has been added to check fermentation; traces of sulphur dioxide may also arise from sulphuring casks or hops.

Allen[3] purifies the hydrochloric acid intended for use in the Marsh test by adding a small quantity of potassium permanganate, and distilling. The distilled acid is quite free from arsenic, but the first fraction coming over contains chlorine and must be rejected. Thorne and Jeffers[4] dilute the acid to 1·1 sp. gr., and gently boil 2 litres of it for an hour with a square of copper gauze, 10 cm. in the side and about 4 meshes to the mm., wrapped round a glass rod. A second piece, and if necessary further pieces of gauze are successively put in, till the gauze remains perfectly bright. The hot acid is transferred to a retort and distilled from a fresh piece of gauze. The first 400 c.c. are rejected and 100 to 200 c.c. are left in the retort. The intermediate acid is free from arsenic. Ling and Rendle[5] effect the purification by boiling hydrochloric acid of constant boiling point, mixed with a small proportion of methyl alcohol, in a reflux apparatus, under reduced pressure, with bright electrolytic copper, free from arsenic; a little arsenic-free granulated zinc is added to the acid. The acid is then distilled over pure copper.

[1] *J. Soc. Chem. Ind.*, 1902, **21**, 675.
[2] *Chem. News*, 1901, **83**, 34.
[3] *J. Soc. Chem. Ind.*, 1902, **21**, 903.
[4] *Proc. Chem. Soc.*, 1902, **18**, 118.
[5] *Analyst*, 1906, **31**, 37.

Other contributions concerning the estimation of minute quantities of arsenic have been made by Lockemann,[1] Mai and Hurt,[2] Bishop,[3] Bertrand and Vamossy,[4] in the report of the Analysis Committee of the International Congress of Applied Chemistry, 1905,[5] and at the joint meeting of the Society of Public Analysts and the Society of Chemical Industry in January 1923.[6]

Dawydow[7] and Berry[8] have shown that selenium affects the delicacy of the test. Rosenheim and Tunnicliffe[9] have drawn attention to the fact that selenium, like arsenic, may give rise to symptoms of poisoning.[10] Rosenheim states that the presence of selenium is not shown by the Marsh test, but that when present with arsenic it influences the size of the arsenic mirror, and may even, under certain conditions, entirely prevent its formation. The Reinsch test may be satisfactorily employed in presence of selenium, provided silver foil is used instead of copper. Further, Bettendorf's test is influenced by the presence of selenium, though the Gutzeit test is not. Schindelmeiser[11] has shown that in the Marsh test selenium, if present, is deposited on the zinc, and that after such deposition is complete arseniuretted hydrogen is evolved and may then be detected as usual.

B. Reinsch's Test.

This test depends on the fact that clean copper when immersed in a hydrochloric acid solution of arsenious acid becomes covered with a grey coating of copper arsenide, As_2Cu_5; the deposit is formed in the cold if much arsenic is present, but only on warming if the solution be dilute. Arsenic acid only gives the reaction on warming. Since antimony also gives a coating of similar appearance, any deposit formed must be specially examined for arsenic (cf. *infra*).

The Reinsch test has now been discarded to a considerable extent, owing to its not being approximately quantitative in character, and also because it is not reliable when the arsenic is present as arsenic acid, or when sulphites are present, and is in point of delicacy inferior to the Marsh-Berzelius or the Gutzeit test. It is, however, of considerable value in certain cases. According to Allen[12] it is preferable to other tests for detecting arsenic in beer, etc. To carry out the reaction he purifies the hydrochloric acid as described above (p. 434), adds a small quantity of the acid and bromine water to 100 c.c. of the beer, boils for a few minutes to oxidise any sulphite present,

[1] *Z. angew. Chem.*, 1905, **18**, 416.
[2] *Z. anal. Chem.*, 1904, **43**, 537.
[3] *J. Amer. Chem. Soc.*, 1906, **28**, 178.
[4] *Chem. Centr.*, 1906, **I.**, 1461.
[5] *Report*, 1906, pp. 280-318.
[6] *Analyst*, 1923, **48**, 63.
[7] *Chem. Centr.*, 1895, **I.**, 811.
[8] *J. Soc. Chem. Ind.*, 1901, **20**, 322.
[9] *Ibid.*, 1901, **20**, 390.
[10] *Chem. News*, 1901, **83**, 280.
[11] *Chem. Centr.*, 1902, **II.**, 960.
[12] *J. Soc. Chem. Ind.*, 1901, **20**, 281.

adds a small quantity of cuprous chloride to reduce the arsenic to the arsenious condition, immerses 1 sq. cm. of copper foil in the solution and boils for half an hour, adding water from time to time to replace that lost by evaporation. If the copper becomes darkened, it is dried on the water-bath, cut into strips, and examined for arsenic by heating one of the strips in a narrow test-tube, and observing whether a sublimate of the characteristic octahedra or tetrahedra of arsenious oxide is formed. Larger crystals are obtained by previously warming the upper portion of the subliming-tube, and the appearance of the crystals may be made more distinct by filling the tube with water. A similar procedure, together with a minute description of the various details involved in carrying out the test, has been published by a committee appointed by the Brewers' Central Association, Manchester;[1] the addition of an oxidising agent to destroy the sulphite and of a reducing agent to convert arsenate to arsenite, is omitted.

C. Gutzeit's Test.

This test is based on the action of arseniuretted hydrogen on solid silver nitrate or mercuric chloride, prepared by allowing a drop of a solution to dry on filter paper, or preferably, according to Eidenbenz, by dissolving a small crystal *in situ* on the paper, and drying. Silver nitrate is first turned yellow, owing to the formation of a compound of silver nitrate with silver arsenide, and subsequently black, owing to separation of metallic silver; mercuric chloride is turned yellow owing to the formation of a mercurous salt having the composition $As(HgCl)_3$. The test is usually performed by placing a small piece of granulated arsenic-free zinc in a test-tube, adding the material to be tested, and then, unless the material itself is acid, a small quantity of dilute sulphuric acid. A plug of cotton wool is placed in the upper part of the tube and the tube capped with the previously prepared piece of filter paper. Sulphuretted hydrogen, phosphoretted hydrogen, and antimoniuretted hydrogen interfere with the reaction. The test is, however, frequently employed in the examination of commercial acids and of other substances; its applications and reliability have been specially studied by Flükiger,[2] Richardson,[3] Gotthelf,[4] Dunstan and Robinson,[5] and Goode and Perkin.[6]

Kirkby's modification[7] of the Gutzeit test, which is frequently employed, is based on the observation that hydrogen sulphide may be completely removed from the evolved gases by means of a 5 per

[1] *J. Soc. Chem. Ind.*, 1901, **20**, 646.
[2] *Arch. Pharm.*, 1889, **27**, 1.
[3] *J. Soc. Chem. Ind.*, 1902, **21**, 901.
[4] *Ibid.*, 1903, **22**, 191.
[5] *Ibid.*, 1904, **23**, 999.
[6] *Ibid.*, 1906, **25**, 507.
[7] *Ibid.*, 1901, **20**, 281.

cent. solution of lead acetate, without any loss of arsenic. The apparatus used for carrying out the test is shown in Fig. 196. The hydrogen is evolved in the flask *a*, and is purified by passing through five bulbs, the three lower being half filled with 5 per cent. lead acetate solution. The purified gas passes into a small funnel, *d*, which is capped with the spotted and dried filter paper.

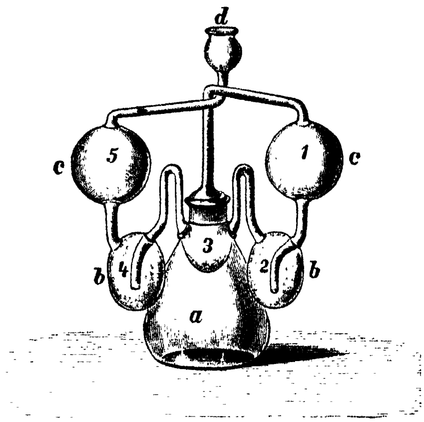

FIG. 196.

Tyrer[1] washes the gas with a 10 per cent. solution of lead acetate in a two-bulb apparatus of different type to the above. A simple form of apparatus, but perhaps not so reliable, has been described by Dowzard.[2]

F. W. Richardson[3] recommends the Gutzeit test, owing to its simplicity as compared with the Marsh test, and the possibility of carrying it out without special precautions.

Hehner[4] objects to this test on the ground that it is impossible to be certain that the stain obtained has been caused by arsenic, since hydrogen phosphide, etc., will also produce similar stains; apart from this, he considers the test very satisfactory and delicate. The method of testing proposed by Bird[5] overcomes Hehner's objection. The stain is treated with boiling hydrochloric acid, whereby a stain produced by phosphoretted hydrogen changes to lemon-yellow, one due to sulphuretted hydrogen disappears, one due to antimoniuretted hydrogen changes to pale grey, whilst that produced by arseniuretted hydrogen changes to brick-red, and may even be recognised when all the gases mentioned are present together in the test. The arsenic stain vanishes on treatment with bromine-hydrochloric acid, and the arsenic may be detected in the resulting solution by means of the brownish-red coloration produced on addition of stannous chloride.

The application of Gutzeit's test to the quantitative estimation of arsenic has been very fully investigated by Sanger and Black.[6] In their apparatus the arsenical hydrogen is passed along the surface of the strip of paper, not perpendicularly against it. Strips of drawing paper of close texture, 4 mm. wide, are drawn through 5 per cent. mercuric chloride solution till thoroughly soaked, then dried and cut

[1] *J. Soc. Chem. Ind.*, 1901, **20**, 281. [2] *Ibid.*, 1900, **19**, 1145.
[3] *Ibid.*, 1902, **21**, 902; *cf.* Gotthelf, *ibid.*, 1903, **22**, 191.
[4] *Ibid.*, 1901, **20**, 194. [5] *Ibid.*, 1901, **20**, 390.
[6] *Ibid.*, 1907, **26**, 1115.

into 7 cm. lengths, and kept in the dark in a bottle containing calcium chloride covered by cotton wool. The generator is a glass bottle about 30 c.c. in capacity, with a rubber cork carrying a short thistle funnel, the outlet of which is constricted to about 1 mm., and a short delivery tube which connects by a cork with a bulb about 12 mm. in diameter carried at the end of a tube about 12 cm. long and 4 mm. clear bore. The bulb is packed with cotton wool which has been kept over sulphuric acid, and the tube contains, next the bulb, a small roll of lead acetate paper, then the strip of sensitised drawing paper. Three g. of uniformly granulated zinc is placed in the bottle, and 15 c.c. of hydrochloric acid (about 1·5 *N*) added by the funnel. After ten minutes a uniform state is reached, and the absence of arsenic from the reagents is established. A known amount of the solution to be tested is now introduced, and the reaction proceeds; after thirty minutes all the arsenic is evolved and the colour on the strip has reached its maximum. The band of colour is then compared with standards made in the same way from solutions containing known amounts (2, 5, 10, etc., micromg.) of arsenious oxide. These standards, if kept in sealed tubes over phosphorus pentoxide, remain constant for several months, but must be renewed from time to time. If the strips be treated for two minutes at (not above) 60° C. with 6 *N* hydrochloric acid, thoroughly washed and dried, the colours are intensified and rendered a little more enduring; or, if they be treated with cold *N*/1 ammonia solution for a few minutes, they develop a black colour of greater length than the original stain, and are greatly increased in endurance, though the dried standards must still be sealed in tubes over quicklime. Antimony compounds should be removed before testing; sulphides are dealt with by the lead acetate paper, and phosphorus compounds do not interfere unless present in very large amount. Arsenates should be reduced by sulphurous acid, and the excess of sulphur dioxide be removed by boiling. The method has a working limit of accuracy of about 1 micromg. (0·001 mg.) of arsenious oxide, though with care $\frac{1}{10}$ of that amount may be detected; and its quantitative results may be looked on as within about 5 per cent. of the truth, provided normal care be taken to preserve all conditions uniform throughout a series of experiments. (The original paper is illustrated by coloured reproductions of the stains on the strips.)

C. Hollins[1] applies the Gutzeit test to the estimation of arsenic in de-arsenicated vitriol. He uses the apparatus shown in Fig. 197, in which the bottle is of 100 c.c. capacity, the bulbs about 2 cm. in diameter, and the tube about 10 cm. long and 3-4 mm. in bore. The bulbs C and D contain a little 10 per cent. lead acetate solution, and

[1] *J. Soc. Chem. Ind.*, 1917, **36**, 576.

E is packed with glass wool wetted with the same solution. He soaks drawing paper for half an hour in a 1 per cent. solution of mercuric chloride, dries it and cuts into strips. In making standards the total volume of arsenic solution and water in the bottle is always 40 c.c., and there are then added 2 c.c. of pure sulphuric acid and 3-4 g. of zinc. In testing de-arsenicated vitriol, 40 c.c. of water is used, 0·5 to 2·0 c.c. of the vitriol, pure sulphuric acid to make up a total of 2·0 c.c., and 3-4 g. of zinc. The further procedure is identical with that of Sanger and Black.

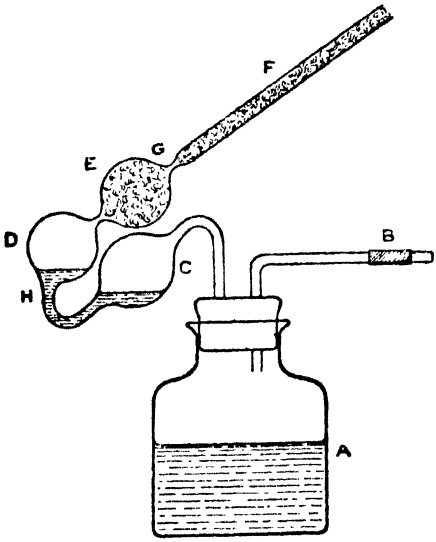

FIG. 197.

D. Bettendorf's Test.

A few drops of the solution to be tested are added to 1 c.c. of concentrated hydrochloric acid, and ½ c.c. of a solution of stannous chloride dissolved in an equal weight of strong hydrochloric acid added to the mixture. If arsenic be present the solution quickly turns brown, and a dark precipitate of metallic arsenic gradually separates out. The change occurs more readily on warming the solution. The reaction does not take place with aqueous solutions of arsenious acid, but only with the arsenious chloride which is formed from it in the presence of strong hydrochloric acid. Hydrogen phosphide and antimoniuretted hydrogen are not reduced by stannous chloride, and consequently do not interfere with the test.

According to Messel,[1] 0·01 mg. As_2O_3 in 1 c.c. sulphuric acid may be detected by this method.

The "tin foil test," which consists in the addition of strong hydrochloric acid to vitriol, then tin foil, and warming the solution, is practically identical with the Bettendorf test.

Other tests have been proposed by Donath[2] and by Seybel and Wikander.[3]

[1] *J. Soc. Chem. Ind.*, 1901, **20**, 192. [2] *Z. anal. Chem.*, 1897, **36**, 664.
[3] *Chem. Zeit.*, 1902, **26**, 50.

Quantitative Determination of Sulphuric Acid and of its Impurities.

Free Sulphuric acid is determined almost exclusively by titration with a standard solution of sodium hydroxide; the gravimetric determination by precipitation as barium sulphate is much less exact, and includes, moreover, any combined sulphuric acid which may be present. On the other hand, the volumetric method includes, as sulphuric acid, other acids present in the free state, but in commercial sulphuric acid the quantity of such other acids may be neglected. The process described on p. 497 must be employed for nitrating and spent acids.

For the volumetric determination, 2 to 3 g. of the acid is weighed off in a bulb pipette (Fig. 201); pipetting concentrated sulphuric acid is precluded by reason of its viscosity. The outside of the pipette is carefully cleaned, the acid then allowed to flow into a relatively large volume of water, and the pipette re-weighed without washing out. The pipette need not be cleaned and dried for further determinations; it suffices to wash it out several times with the fresh acid to be tested.

Working with the quantity of acid given above, it is best to titrate with normal sodium hydroxide solution. The most satisfactory indicator is methyl orange, used sparingly (*cf.* p. 39), at the ordinary temperature and not in a warm solution. The amount of nitrous acid present in commercial vitriol does not interfere with the titration, but when larger quantities are present excess of standard alkali must be added and the liquid titrated back with standard acid.

Sulphurous acid, if present in appreciable quantity, is best determined by means of iodine (p. 401). Should nitrogen acids be present, sulphurous acid can only exist in traces, and cannot in such cases be determined quantitatively.

Nitrous acid (Nitrosyl-sulphuric acid), if present to any considerable extent, is determined by potassium permanganate (p. 412). Such small amounts as cannot be determined with certainty either by permanganate or by the nitrometer, may be estimated colorimetrically. Of the various methods proposed for this purpose, that in which the modified Griess reagent (α-naphthylamine and sulphanilic acid) is used, is the best.[1]

Lunge and Lwoff[2] found that a large excess of this reagent is necessary in order to obtain reliable colorimetric results, and that in the absence of such excess the intensity of the coloration increases much less rapidly than the percentage of nitrous acid present. Under suitable conditions and with at least one hundred times the quantity of reagent

[1] Ilosvay, *Bull. Soc. Chem.*, 1894, **11**, 216.

[2] *Z. angew. Chem.*, 1894, **7**, 348; the whole of the literature relating to the subject is given in this paper.

theoretically necessary, the intensity of the coloration corresponds to the percentage of nitrous acid. By observing the details given below for the preparation of fresh reagent, the addition of 1 c.c. suffices in all cases to which the colorimetric method is applicable—that is, to dilute solutions.

As is well known, the red coloration produced by the action of very minute traces of nitrous acid only appears after some time, and increases in intensity for several hours. This might appear to be a drawback in the application of the test for colorimetric determinations, but it is not really so, for if all conditions, more particularly the time allowed for reaction, are equal, the colour intensity and percentage of nitrous acid remain comparable. If it be desired, therefore, to compare a solution of unknown strength with a known standard solution, it is only necessary to treat both with the reagent at the same time; the comparison may then be made either at the end of five minutes, or of half an hour, or after twenty-four hours, and always with the same result; for though the absolute colour intensity continually increases, the relative values remain the same.

In the case of aqueous solutions the comparison may usually be made immediately, or at all events in a quarter of an hour, after the addition of the reagent. The presence of free mineral acid even in traces retards the reaction and renders the coloration less intense; a large amount entirely stops the reaction. This is due to the fact that the coupling of diazonium compounds is more or less inhibited by the presence of mineral acids. This difficulty is readily and completely overcome by adding sodium acetate in sufficient quantity to take up the whole of the mineral acid. The sodium acetate employed must, of course, give no coloration with the reagent. A "normal solution" for purposes of comparison must be prepared for the test. Dilute aqueous solutions of sodium nitrite are not suitable, owing to their instability. The nitrous acid is therefore employed in the form of the perfectly stable nitrosyl-sulphuric acid, and the "normal solution" is prepared by dissolving 0·0493 g. pure sodium nitrite (= 10 mg. N) in 100 c.c. of water and adding 10 c.c. of the solution to 90 c.c. of pure sulphuric acid; the solution thus contains 1/100 mg. of nitrite nitrogen per c.c.

In carrying out the test, 1 c.c. of the "reagent" diluted with about 40 c.c. of water is placed in each of two colorimeter cylinders; to the one is added 5 g. of solid sodium acetate and 1 c.c. of the "normal solution," to the other, 5 g. sodium acetate and 1 c.c. of the acid to be tested, and the whole well mixed so that the nitrous acid may react with the reagent at the moment of liberation. The colorations produced may be compared when desired; as a rule, five minutes' standing will prove sufficient. It is unnecessary and disadvantageous

to warm the solutions, which are best mixed by means of glass tubes blown below into a bulb corresponding to the inside diameter of the cylinders, as in the Nessler test for ammonia; by moving these stirrers up and down three or four times efficient mixing is secured.

The "reagent" is prepared by dissolving 0·100 g. pure white α-naphthylamine in 100 c.c. of water by boiling for one-quarter hour, adding to this solution 5 c.c. of glacial acetic acid, or the equivalent quantity of weaker acetic acid, followed by a solution of 1 g. of sulphanilic acid in 100 c.c. of water. The mixture must be kept in well-stoppered bottles. The solution readily discolours, but a faint rose coloration may be disregarded since it disappears when 1 c.c. of the reagent is diluted to the 50 c.c. used in the test; any stronger coloration may be removed by reducing the solution with zinc dust. One c.c. of the reagent will, after ten minutes, indicate distinctly the presence of 1/1000 mg. nitrite nitrogen in 100 c.c. of water.

Nitric acid.—According to Lunge and Lwoff, the brucine reaction may be employed for the colorimetric estimation of nitric acid alone, if the comparisons be made not with the initial red coloration but with the sulphur-yellow colour, which appears later. The solutions required are:—(1) a brucine solution prepared by dissolving 0·2 g. brucine in 100 c.c. of pure concentrated sulphuric acid; and (2) a normal solution of potassium nitrate containing $\frac{1}{100}$ mg. nitric nitrogen per c.c., prepared by dissolving 0·0722 g. of the pure salt in 100 c.c. of distilled water and making 10 c.c. of this stock solution up to 100 c.c. with pure concentrated sulphuric acid. These solutions are best kept in well-stoppered burettes fitted with glass taps; that intended for the "normal" solution should be graduated in $\frac{1}{20}$ c.c.

The sulphuric acid to be tested may be used directly, provided it is of not less than 1·7 sp. gr.; weaker solutions or acids must be mixed, in measured ratio, with pure concentrated sulphuric acid until the above strength is approximately attained (*cf.* p. 432); thus water alone will require the addition of three times its volume of concentrated acid.

Narrow 50 c.c. graduated cylinders of pure white glass are employed in comparing the colours; the graduated portion should be about 24 cm. in length, and the cylinder should extend a further 10 cm. beyond the last graduation mark, to allow for mixing. The Hehner cylinders, which are furnished with side taps at a height of about 5 cm. from the bottom, are very convenient. An actual colorimeter will, of course, give the most accurate results (*cf.* p. 181).

The test is made as follows:—1 c.c. of the normal solution and 1 c.c. of brucine solution are placed in one of the cylinders and pure concentrated sulphuric acid added up to the 50 c.c. mark; the mixture is

then transferred to a flask and heated to 70° to 80°. When the colour has changed to sulphur yellow the solution is cooled and returned to the cylinder. The solution to be tested is treated similarly, either alone or after admixture with more concentrated sulphuric acid, as ascertained by a preliminary test. Part of the solution is then poured away, or run off through the side tap, from one or other of the cylinders until the depth of colour is the same in each; the result is then obtained in the usual way by calculation from the measure of normal solution required per given volume of the unknown solution.

Selenious acid, according to Lunge,[1] has no effect on brucine.

In the presence of appreciable quantities of iron salts such as may occur, for example, in certain makes of concentrated sulphuric acid, the brucine test is less delicate, and the colour changes produced are not identical even when equal quantities of nitric acid are present.

Lead.—Concentrated acids are diluted with an equal volume of water and twice the volume of alcohol, and allowed to stand for some time. The precipitated lead sulphate is filtered off, washed with dilute alcohol, dried, and ignited. The precipitate should be separated from the filter paper as completely as possible; the paper must not be burnt off in a platinum crucible. 1 g. $PbSO_4$ = 0·6832 g. Pb.

Iron.—If the quantity present is not too small, titration with permanganate may be employed after first reducing the iron to the ferrous state. This reduction may be carried out in many ways. The most usual method is by means of chemically pure zinc, which should always be tested for freedom from iron, the reduction being hastened by warming, and carried out in a flask fitted with a Bunsen valve, or still better with a Contat bulb (Fig. 20, p. 63), or, according to Winkler, by wrapping a zinc rod with platinum wire. The reduction is complete when a drop of the solution, withdrawn by the aid of a capillary tube, produces no red coloration with potassium thiocyanate. The solution is allowed to cool, poured through a funnel provided with a platinum cone or nearly closed by a glass stopper (not through filter paper), to keep back the zinc, the flask and undissolved zinc washed with thoroughly boiled, air-free water, and the solution titrated. Should the zinc contain iron, a blank experiment must be made on at least 3 g. of the zinc, a weighed quantity of this taken for the reduction, and the operation continued until all the zinc has been dissolved.

Skrabal[2] employs about one hundred parts of zinc for each part of iron present, from which it will be seen that the smallest trace of iron in the zinc may lead to very appreciable error. Any titanic acid present will also be reduced by the zinc, and must consequently be taken into account.

[1] *Ber.*, 1887, **20**, 2031. [2] *Z. anal. Chem.*, 1903, **42**, 359.

Ebeling[1] proposes to add a little thiocyanate to the iron solution itself in order to ascertain when reduction is complete, the heating being continued until the red coloration has disappeared. Volhard[2] has shown that this is unsuitable, partly because the thiocyanate is destroyed in the process, and partly because traces of iron require a comparatively large excess of thiocyanate for their detection. Other methods of reduction possess no advantages over the use of zinc for this purpose.

In the foregoing and analogous cases it is advisable to use $N/20$ potassium permanganate solution, prepared by diluting the seminormal solution (p. 59); 1 c.c. will correspond to 0·002792 g. Fe. Further, a considerable quantity of the acid, say 50 c.c., should be employed for the test, since as a rule the quantity of iron present is very small.

For very small amounts of iron the colorimetric ferric thiocyanate method may be employed. It is scarcely possible to obtain nitric acid absolutely free from iron for oxidising the iron in the solution to be tested to the ferric state, but this difficulty may be overcome by employing as pure an acid as possible, working only with small quantities, and making a blank test for comparison. The best results are obtained under the following conditions worked out by Lunge.[3]

Glass-stoppered 25 c.c. cylinders of perfectly colourless glass, graduated in $\frac{1}{10}$ c.c. divisions, are employed in the test. The total height of each cylinder is 17 cm. and the internal diameter 13 mm.; to facilitate mixing, the graduated portion does not reach beyond a point 5 cm. below the stopper. The cylinders should be as similar in size as possible, so that equal volumes reach to the same height in each. At least three cylinders are required; it is preferable to have four or six. The necessary reagents are: (1) a 10 per cent. solution of potassium thiocyanate; (2) pure ether; (3) a solution of ammonium iron alum prepared by dissolving 8·634 g. iron alum in a litre of water, and diluting 1 c.c. of this solution to 100 c.c.; the solution will thus contain 0·010 g. Fe per litre. This dilute solution soon decomposes, especially in the light, and can only be kept for a few days even in a dark place. The stronger solution, containing the 8·634 g. iron alum per litre, may be kept for a considerable time if protected from air and light, and if, in preparing the solution, 5 c.c. of pure concentrated sulphuric acid is added before filling to the litre mark. The quantity of sulphuric acid thus introduced into the test scarcely amounts to 1 mg., and is therefore negligible; (4) pure nitric acid as above.

Fifty c.c. of the diluted sulphuric acid is taken for the test and first oxidised by warming with exactly 1 c.c. of nitric acid. At the same

[1] *Z. angew. Chem.*, 1901, 14, 571.
[2] *Ibid.*, 1901, 14, 609.
[3] *Ibid.*, 1896, 9, 3.

time a second 1 c.c. of nitric acid (4) is diluted to 50 c.c. with distilled water. Should the experiment indicate later that the sulphuric acid solution should be still further diluted, the nitric acid solution must also be diluted to the same extent, so that in both cases the amount of iron introduced with the nitric acid will be the same. Any nitric acid which produces more than a very faint reddish tinge with the thiocyanate solution must be rejected.

Exactly 5 c.c. of the prepared solution of the sulphuric acid to be tested is then placed in one of the stoppered cylinders (A), and 5 c.c. of the diluted nitric acid in a second cylinder (B). To the latter a suitable quantity, say 1 c.c. of the iron alum solution, is then added from a burette, and to A an equal volume of water, so that the solutions in the two cylinders are brought to the same dilution. Five c.c. of the thiocyanate solution are next added to each solution. Both mixtures will redden, but the coloration is frequently of a somewhat dirty yellowish red, and its intensity bears no relationship to the iron content of the solution. Finally, 10 c.c. of ether is added to each cylinder and the contents thoroughly agitated. The aqueous solution contains a double thiocyanate of potassium and iron. This double salt is split up on shaking with ether, which dissolves only or preferably the iron thiocyanate, as is evidenced by the rose-red coloration of the ethereal solution as compared with the yellowish red of the aqueous solution. Shaking must be continued until the aqueous layer becomes colourless. The ethereal solution gradually darkens in colour, presumably owing to a further splitting up of the double thiocyanate; the solutions should therefore be prepared in rapid sequence, and preferably only compared after standing for several hours.

Differences of considerable magnitude are detected immediately, so that it only becomes necessary to employ, in addition to the cylinder A, containing the sulphuric acid solution, two other cylinders, B and C, to which have been added the approximately correct quantities of iron alum solution; the final comparison, however, is, as stated, not made for some hours. The solutions should not be allowed to stand too long, for instance, over night, for it sometimes happens that after long standing the ether becomes nearly, or even perfectly, colourless, only a strongly coloured narrow zone of liquid remaining at the dividing line between the ether and the water. This only occurs occasionally, and is to be attributed to traces of impurities present in such extremely small quantities that they cannot be identified.

The degree of accuracy of the method may readily be brought to $\pm 0{\cdot}1$ c.c. iron alum solution, that is, to $\pm 0{\cdot}000001$ g. Fe, on the 5 c.c. of solution taken, provided the volume of alum solution used does not exceed 2 c.c., equivalent to 0·00002 g. Fe. That is, the reading may be made to 1/20 of the total iron present; this may be looked upon as

satisfactory, where only thousandths or hundredths of a per cent. come into account. It is not, however, sufficient for appreciably greater amounts, and for such the volumetric method must be employed.

The above degree of accuracy may be attained without difficulty by merely examining the ethereal layer by transmitted light. The comparison may be made more accurate by looking through the ethereal layer obliquely from above, or by holding the cylinders a little above a white surface, and looking through the full depth of liquid in the cylinder. This plan is much better than allowing the cylinders to stand on the white surface. Colorimeters, as ordinarily constructed, are not suited for this particular determination, no provision being made for shaking, preventing loss of ether, etc., but one specially suitable for this purpose has been described by Stokes and Cain.[1] Seyda[2] has described a method differing but little from the above, and intended for use in the examination of water.

Hydrochloric acid.—Ten c.c. of the acid is boiled in a small flask and the vapours evolved conducted to the surface of water contained in a second flask. The hydrochloric acid is dissolved by the water, and may be determined by titration with alkali or with $N/10$ silver nitrate solution.

Arsenic.—About 20 g. of the acid is diluted with water, the solution filtered from any precipitated lead sulphate, and then treated with a current of sulphurous anhydride until the solution smells strongly of the gas, to reduce all arsenic compounds to the arsenious condition. Prolonged action and a considerable excess of sulphur dioxide are necessary for the reduction. The excess of sulphur dioxide is removed by heating, aided by a current of carbon dioxide, the solution exactly neutralised by addition of sodium carbonate and bicarbonate, and titrated with $N/10$ iodine and starch solution till the colour change to blue occurs. One c.c. of the iodine solution corresponds to 0·00495 g. As_2O_3. Iron must first be removed should it be present in appreciable quantity.

The presence of lead, antimony, copper, platinum, etc., somewhat complicates the determination.[3]

According to Böckmann, the reduced solution, freed from excess of sulphur dioxide as above, is treated for some hours at a moderate temperature with a current of sulphuretted hydrogen, which precipitates the arsenic and other metals which yield sulphides insoluble in acid solution. The precipitate is filtered off and well washed, at first with water rendered slightly acid with hydrochloric acid, and then with hot water until the washings leave no residue when evaporated on platinum foil. The precipitate, which contains arsenic sulphide and antimony

[1] *J. Amer. Chem. Soc.*, 1909, **29**, 409. [2] *Chem. Zeit.*, 1898, **22**, 1086.
[3] L. M'Cay, *J. Amer. Chem. Soc.*, 1885, **7**, 6.

sulphide, is dried and weighed. It is then moistened with cold water and, when thoroughly damped, extracted with dilute ammonia. The residue remaining on the filter, consisting of sulphur and antimony sulphide, is washed with hot water, dried, and weighed as above. The difference between the two weights gives the content of arsenic sulphide sufficiently accurately for technical purposes.

Hattensaur[1] uses a modification of the same method. Very minute quantities of arsenic are estimated approximately by the Marsh-Berzelius or the Gutzeit test (*cf.* p. 433 *et seq.*).

Fuming Sulphuric Acid (Anhydride, Oleum)

Fuming sulphuric acid is generally regarded as a solution of sulphur trioxide (sulphuric anhydride, SO_3) in sulphuric acid monohydrate (H_2SO_4). As a matter of fact, the chief constituent is generally pyrosulphuric acid ($H_2S_2O_7$), and the so-called 45 per cent. oleum consists entirely of this. The other varieties below 45 per cent. are mixtures of pyrosulphuric acid with monohydrate, and those above 45 per cent. mixtures of pyrosulphuric acid with anhydride. The strength is always given as percentage of anhydride, no account being taken of the presence of pyrosulphuric acid. The latter is looked upon, from the analytical standpoint, as a mixture of fifty-five parts H_2SO_4 with forty-five parts SO_3.

Properties of fuming sulphuric acid. Pyrosulphuric acid, $H_2S_2O_7$, and those acids near to it in composition, that is acids from slightly below 40 per cent. up to nearly 60 per cent. SO_3, are solid ; those ranging from 0 to nearly 40 per cent., and from 60 per cent. to 70 per cent. SO_3 are oily liquids. From 70 per cent. upwards the oleum is once more solid, until it finally passes to pure anhydride.

Melting Points of Oleum. Knietsch.[2]

Per cent. SO_3.	Melting Point.	Per cent. SO_3.	Melting Point.	Per cent. SO_3.	Melting Point.
0	+10	35	+26·0	70	+ 9·0
5	+ 3·5	40	+33·8	75	+17·2
10	- 4·8	45	+34·8	80	+20·0
15	-11·2	50	+28·5	85	+33·0 (27·0)[1]
20	-11·0	55	+18·4	90	+34·0 (27·7)
25	- 0·6	60	+ 0·7	95	+36·0 (26·0)
30	+15·2	65	+ 0·8	100	+40·0 (17·7)

[1] *Z. angew. Chem.*, 1896, **9**, 130.

[2] *Ber.*, 1901, **34**, 4100. The figures in brackets are the melting points of the fresh non-polymerised acids.

Boiling Points of Oleum. Knietsch.[1]

SO_3, Total, per cent.	SO_3, Free, per cent.	Boiling Point.	Barometric Pressure, Mm.
82·3	3·64	212	759
83·4	9·63	170	759
86·45	26·23	125	759
89·5	42·84	92	759
93·24	63·20	60	759
99·5	97·2	43	759

Specific Gravity of Fuming Sulphuric Acid at 35° C. Knietsch.[2]

Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.	Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.
81·63	0	1·8186	91·18	52	1·9749
81·99	2	1·8270	91·55	54	1·9760
82·36	4	1·8360	91·91	56	1·9772
82·73	6	1·8425	92·28	58	1·9754
83·09	8	1·8498	92·65	60	1·9738
83·46	10	1·8565	93·02	62	1·9709
83·82	12	1·8627	93·38	64	1·9672
84·20	14	1·8692	93·75	66	1·9636
84·56	16	1·8756	94·11	68	1·9600
84·92	18	1·8830	94·48	70	1·9564
85·30	20	1·8919	94·85	72	1·9502
85·66	22	1·9020	95·21	74	1·9442
86·03	24	1·9092	95·58	76	1·9379
86·40	26	1·9158	95·95	78	1·9315
86·76	28	1·9220	96·32	80	1·9251
87·14	30	1·9280	96·69	82	1 9183
87·50	32	1·9338	97·05	84	1·9115
87·87	34	1·9405	97·42	86	1·9046
88·24	36	1·9474	97·78	88	1·8980
88·60	38	1·9534	98·16	90	1·8888
88·97	40	1·9584	98·53	92	1·8800
89·33	42	1·9612	98·90	94	1·8712
89·70	44	1·9643	99·26	96	1·8605
90·07	46	1·9672	99·63	98	1·8488
90·44	48	1 9702	100·00	100	1·8370
90·81	50	1·9733	...	...	...

This table may be used in calculating the quantity of concentrated sulphuric acid to be added to an oleum to obtain an oil of any desired lower strength in free SO_3. Gerster[3] gives the following formula for this purpose:—

$$x = 100 \frac{b-a}{a-c}$$

where x represents the quantity of sulphuric acid to be added to 100 parts of the oleum, a the total SO_3 per 100 parts of the acid desired,

[1] *Ber.*, 1901, 34, 4110. [2] *Ibid.*, 4101.
[3] *Chem. Zeit.*, 1887, 11, 3.

Table of Density and Composition of

Density 20°/4°.	Δ	Free SO_3.	H_2SO_4.	H_2O.	Total SO_3.	Total H_2SO_4.	Acid of 65·5 B.	Acid of 60 B.	Acid of 53 B.	Acid of 50 B.	Oleum 20 per cent.	Oleum 30 per cent.	Oleum 60 per cent.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1·8390	41	0	100	18·367	81·633	100·000	74·85	50·60	40·50	37·51	0	0	0
1·8431	41	1	99	18·184	81·816	100·225	74·10	50·09	40·10	37·14	5	3·33	1·67
1·8472	40	2	98	18·000	82·000	100·450	73·35	49·59	39·69	36·76	10	6·67	3·33
1·8512	40	3	97	17·816	82·184	100·675	72·60	49·08	39·29	36·39	15	10·00	5·00
1·8552	39	4	96	17·633	82·367	100·900	71·85	48·58	38·88	36·02	20	13·33	6·67
1·8591	39	5	95	17·449	82·551	101·125	71·10	48·07	38·48	35·64	25	16·67	8·33
1·8630	39	6	94	17·265	82·735	101·350	70·35	47·56	38·07	35·26	30	20·00	10·00
1·8669	38	7	93	17·082	82·918	101·575	69·61	47·06	37·66	34·89	35	23·33	11·67
1·8707	38	8	92	16·898	83·102	101·800	68·86	46·55	37·26	34·51	40	26·67	13·33
1·8745	37	9	91	16·714	83·286	102·025	68·11	46·04	36·86	34·13	45	30·00	15·00
1·8782	37	10	90	16·531	83·469	102·250	67·36	45·54	36·45	33·76	50	33·33	16·67
1·8819	37	11	89	16·347	83·653	102·475	66·61	45·03	36·05	33·39	55	36·67	18·33
1·8856	36	12	88	16·163	83·837	102·700	65·86	44·53	35·65	33·01	60	40·00	20·00
1·8892	36	13	87	15·980	84·020	102·925	65·11	44·02	35·24	32·64	65	43·33	21·67
1·8928	35	14	86	15·796	84·204	103·150	64·36	43·52	34·83	32·26	70	46·67	23·33
1·8963	35	15	85	15·612	84·388	103·375	63·62	43·01	34·43	31·89	75	50·00	25·00
1·8998	35	16	84	15·429	84·571	103·600	62·87	42·50	34·02	31·51	80	53·33	26·67
1·9033	34	17	83	15·245	84·755	103·825	62·12	42·00	33·62	31·14	85	56·67	28·33
1·9067	34	18	82	15·061	84·939	104·050	61·37	41·49	33·21	30·76	90	60·00	30·00
1·9101	33	19	81	14·878	85·122	104·275	60·63	40·99	32·81	30·39	95	63·33	31·67
1·9134	33	20	80	14·694	85·306	104·500	59·88	40·48	32·40	30·01	100	66·67	33·33
1·9167	33	21	79	14·510	85·490	104·725	59·13	39·97	32·00	29·64	98·75	70·00	35·00
1·9200	32	22	78	14·327	85·673	104·950	58·38	39·47	31·60	29·26	97·50	73·33	36·67
1·9232	32	23	77	14·143	85·857	105·175	57·63	38·96	31·19	28·89	96·25	76·67	38·33
1·9264	31	24	76	13·959	86·041	105·400	56·88	38·45	30·78	28·51	95·00	80·00	40·00
1·9295	31	25	75	13·776	86·224	105·625	56·14	37·95	30·38	28·14	93·75	83·33	41·67
1·9326	31	26	74	13·592	86·408	105·850	55·39	37·44	29·97	27·76	92·50	86·67	43·33
1·9357	30	27	73	13·408	86·592	106·075	54·63	36·93	29·57	27·39	91·25	90·00	45·00
1·9387	30	28	72	13·224	86·776	106·300	53·89	36·43	29·16	27·01	90·00	93·33	46·67
1·9417	29	29	71	13·041	86·959	106·525	53·14	35·93	28·76	26·64	88·75	96·67	48·33
1·9446	29	30	70	12·857	87·143	106·750	52·39	35·42	28·35	26·26	87·50	100·00	50·00
1·9475	29	31	69	12·673	87·327	106·975	51·64	34·91	27·94	25·88	86·25	98·57	51·67
1·9504	28	32	68	12·490	87·510	107·200	50·90	34·41	27·54	25·51	85·00	97·15	53·33
1·9532	28	33	67	12·306	87·694	107·425	50·15	33·90	27·14	25·13	83·75	95·71	55·00
1·9560	27	34	66	12·122	87·878	107·650	49·40	33·39	26·73	24·76	82·50	94·28	56·67
1·9587		35	65	11·939	88·061	107·875	48·65	32·89	26·33	24·39	81·25	92·86	58·33

[1] *Monit. Scient.*, 1913,

Fuming Sulphuric Acid of 20° C. Gavelle.[1]

Oleum 70 per cent.	1 Litre contains in Kilogrammes.												
	Free SO_3.	H_2SO_4.	H_2O.	Total SO_3.	Total H_2SO_4.	Acid of 65·3 B.	Acid of 63 B.	Acid of 53 B.	Acid of 50 B.	Oleum 20 per cent.	Oleum 30 per cent.	Oleum 60 per cent.	Oleum 70 per cent.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent	Per cent.	Per cent.	Per cent.
0	0·000	1·839	0·338	1·501	1·839	1·376	0·931	0·745	0·690	0·000	0·000	0·000	0·000
1·43	0·018	1·825	0·335	1·508	1·847	1·366	0·923	0·739	0·685	0·092	0·061	0·031	0·026
2·86	0·037	1·810	0·332	1·515	1·856	1·355	0·916	0·733	0·679	0·185	0·123	0·062	0·053
4·29	0·056	1·796	0·330	1·521	1·864	1·344	0·909	0·727	0·674	0·278	0·185	0·093	0·079
5·71	0·074	1·781	0·327	1·528	1·872	1·333	0·901	0·721	0·668	0·371	0·247	0·124	0·106
7·14	0·093	1·766	0·324	1·535	1·880	1·322	0·894	0·715	0·663	0·465	0·310	0·155	0·133
8·57	0·112	1·751	0·322	1·541	1·888	1·311	0·886	0·709	0·657	0·559	0·373	0·186	0·160
10·00	0·131	1·736	0·319	1·548	1·896	1·300	0·879	0·703	0·651	0·653	0·436	0·218	0·187
11·43	0·150	1·721	0·316	1·555	1·904	1·288	0·871	0·697	0·646	0·748	0·499	0·249	0·214
12·86	0·169	1·706	0·313	1·562	1·912	1·277	0·863	0·691	0·640	0·844	0·562	0·281	0·241
14·29	0·188	1·690	0·310	1·568	1·920	1·265	0·855	0·685	0·634	0·939	0·626	0·313	0·268
15·71	0·207	1·675	0·308	1·574	1·928	1·254	0·847	0·678	0·628	1·035	0·690	0·345	0·296
17·14	0·226	1·659	0·305	1·581	1·936	1·242	0·840	0·672	0·622	1·131	0·754	0·377	0·323
18·57	0·246	1·644	0·302	1·587	1·944	1·230	0·832	0·666	0·617	1·228	0·819	0·409	0·351
20·00	0·265	1·628	0·299	1·594	1·952	1·218	0·824	0·659	0·611	1·325	0·883	0·442	0·379
21·43	0·284	1·612	0·296	1·600	1·960	1·206	0·816	0·653	0·605	1·422	0·948	0·474	0·406
22·86	0·304	1·596	0·293	1·607	1·968	1·194	0·807	0·646	0·598	1·520	1·013	0·507	0·434
24·29	0·324	1·580	0·290	1·613	1·976	1·182	0·799	0·640	0·593	1·618	1·079	0·539	0·462
25·71	0·343	1·563	0·287	1·620	1·984	1·170	0·791	0·633	0·587	1·716	1·144	0·572	0·490
27·14	0·363	1·547	0·284	1·626	1·992	1·158	0·783	0·627	0·580	1·815	1·210	0·605	0·518
28·57	0·383	1·531	0·281	1·632	2·000	1·146	0·775	0·620	0·574	1·913	1·276	0·638	0·547
30·00	0·403	1·514	0·278	1·639	2·007	1·133	0·766	0·613	0·568	1·893	1·342	0·671	0·575
31·43	0·422	1·498	0·275	1·645	2·015	1·121	0·758	0·607	0·562	1·872	1·408	0·704	0·603
32·86	0·442	1·481	0·272	1·651	2·023	1·108	0·749	0·600	0·556	1·851	1·475	0·737	0·632
34·29	0·462	1·464	0·269	1·657	2·030	1·096	0·741	0·593	0·549	1·830	1·541	0·771	0·660
35·71	0·482	1·447	0·266	1·663	2·038	1·083	0·732	0·586	0·543	1·809	1·608	0·804	0·689
37·14	0·502	1·430	0·263	1·670	2·046	1·070	0·724	0·579	0·536	1·788	1·675	0·837	0·718
38·57	0·523	1·413	0·260	1·676	2·053	1·057	0·715	0·572	0·530	1·766	1·742	0·871	0·747
40·00	0·543	1·396	0·256	1·683	2·061	1·045	0·706	0·565	0·524	1·745	1·809	0·905	0·775
41·43	0·563	1·379	0·253	1·689	2·068	1·032	0·698	0·558	0·517	1·723	1·877	0·938	0·804
42·86	0·583	1·361	0·250	1·695	2·076	1·019	0·689	0·551	0·511	1·702	1·945	0·972	0·833
44·29	0·604	1·344	0·247	1·701	2·083	1·006	0·680	0·544	0·504	1·680	1·920	1·006	0·863
45·71	0·624	1·326	0·244	1·707	2·091	0·993	0·671	0·537	0·498	1·658	1·895	1·040	0·892
47·14	0·645	1·309	0·240	1·713	2·098	0·980	0·662	0·530	0·492	1·636	1·869	1·074	0·921
48·57	0·665	1·291	0·237	1·719	2·106	0·966	0·653	0·523	0·484	1·614	1·844	1·108	0·950
50·00	0·686	1·273	0·234	1·725	2·113	0·953	0·644	0·516	0·478	1·591	1·819	1·143	0·979

[1] 3, Part I., 301.

b the total SO_3 per 100 parts of the original strong oleum, and *c* the SO_3 per 100 parts of the acid used for dilution. The values for *a* and *b* are taken from the table; *c* is obtained by multiplying the percentage of H_2SO_4 present in the acid used for dilution by 0·816. See also Prats.[1]

Impurities. These may be the same as those present in ordinary sulphuric acid, but since fuming acid is now made exclusively by the contact process, they will only occur in inconsiderable quantity. The examination for these impurities is carried out exactly as in the case of ordinary sulphuric acid (p. 429 *et seq.*).

Quantitative Analysis of Fuming Sulphuric Acid.[2]

The sampling of oleum is a matter of some difficulty. With liquid oleum, or with the partially or completely crystalline products up to 45 per cent. SO_3, which may be liquefied without danger by warming to 30° in closed vessels on the sand-bath, the difficulty is not very great. In works the soldered leaden vessels containing the acid are usually stored in a warmed room, so that the contents are always liquid. It is advisable to remove the stopper or other seal before warming, and to substitute a watch-glass; this does not cause any appreciable loss of SO_3 and checks the development of pressure, which might easily lead to an accident on removing the stopper.

Products rich in SO_3 cannot be completely liquefied by warming. A jelly-like residue always remains, but as this possesses the same composition as the liquefied portion, the sample may be drawn from the latter.

The portion for analysis is taken from these larger samples.

Solid oleum (pyrosulphuric acid) must be liquefied in the sample bottle by gently warming, before being withdrawn by the pipette for analysis; it will then remain liquid sufficiently long to allow of its flowing from the pipette even after weighing. Actual anhydride and oleum approaching this strength cannot be handled in this manner, as they fume too much. In such cases Stroof's method may be followed. This consists in weighing several portions of the anhydride in a glass-stoppered bottle, and then adding a weighed quantity of accurately analysed monohydrate sufficient to produce an oleum of about 70 per cent., which is liquid at the ordinary temperature. Solution is

[1] *Chem. Zeit.*, 1910, **34**, 264.

[2] *Cf.* Fürstenau, *Chem. Zeit.*, 1880, **4**, 18; Möller, *ibid.*, 1880, **4**, 569; Becker, *ibid.*, 1880, **4**, 600; Winkler, *Chem. Ind.*, 1880, **3**, 194; Clar and Gaier, *ibid.*, 1881, **4**, 251; Rosenlecher, *Z. anal. Chem.*, 1898, **37**, 209; Setlik, *Chem. Zeit.*, 1889, **13**, 1670; Rabe, *Chem. Zeit.*, 1901, **15**, 345; *Sulphuric Acid and Alkali*, **1**, p. 358 *et seq.*

hastened by warming to 30° to 40° with the stopper placed loosely in the bottle. The analysis of the mixture is then carried out in the ordinary way.

The value of an oleum depends chiefly on the content of free anhydride, SO_3; the results are accordingly calculated in the following manner. First, the total acidity is determined by titration and calculated to SO_3; the difference between 100 and the percentage so obtained is regarded as water, for each 18·1 parts of which 80·06 parts SO_3 are necessary for the formation of H_2SO_4; after all water has been allowed for in this way, any SO_3 remaining is taken as free anhydride. It must not, however, be forgotten that other substances may be present in addition to the water, especially sulphurous acid, SO_2, which, as will subsequently be seen, considerably affects the result. Solid constituents, in more than traces, are also occasionally present; these must be determined and the percentages obtained deducted from the water value, otherwise the result obtained for the percentage of free SO_3 will be too low.

The analysis of fuming sulphuric acid or anhydride is carried out as follows:—

The oleum is weighed off in tared, thin-walled bulb tubes of about 20 mm. diameter, drawn out at both ends to form long capillaries. Three to 5 g. of the melted, completely homogeneous oleum, which is sufficient nearly to half-fill the tube, is drawn in by the following device. An ordinary narrow-necked flask is fitted with a rubber stopper, through which passes a well-ground glass tap provided with a piece of rubber tubing at its free end. A partial vacuum is produced in the flask by suction (with the mouth), the tap closed, the rubber tube passed over one of the capillaries of the weighing bulb, and the other capillary immersed in the oleum; on opening the tap the desired quantity of oleum is drawn into the bulb.

The bulb is then cleaned, one of the capillary ends sealed by fusion, and the whole weighed. Loss of anhydride by evaporation or absorption of moisture through the non-sealed, capillary end does not occur to any appreciable extent during the weighing. In weighing, it is advisable to support the capillary ends of the bulb-tube on a small platinum crucible with two notches cut in the rim; this will prevent damage to the balance should breakage occur.

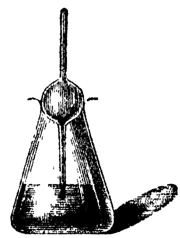

FIG. 198.

The weighed bulb is then placed in a small Erlenmeyer flask (Fig. 198), so that the bulb closes the neck and the point of the open capillary dips rather deeply into the water contained in the flask. By this means any loss of anhydride by evaporation is excluded. The point of the upper capillary is then broken, and after all the oleum has

run out the tube is washed by dropping water through the upper capillary, and finally by sucking in water several times so as to fill the bulb completely. The solution is diluted to 500 c.c. and 50 c.c. taken for titration. The titration is made with $N/5$ sodium hydroxide solution (1 c.c. = 0·008 g. SO_3), using methyl orange as indicator (not litmus). Sulphurous acid is determined by titrating a second portion of the solution with iodine solution, and the quantity found deducted from the total acidity, as found in the titration with alkali.

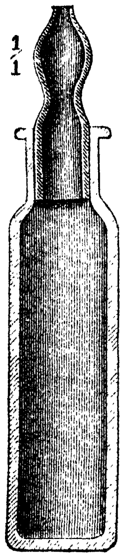

FIG. 199.

Clar and Gaier weigh the anhydride (oleum) in a glass bottle (Fig. 199), 58 mm. high and 17 mm. wide, fitted with a long, ground-in glass stopper broadened out to a bulb above the neck of the bottle, and pierced on the top with a small hole which can be closed by a small glass stopper. The interior of the stopper is filled with glass wool moistened slightly with water. Two to 3 g. of the melted anhydride or fuming acid is introduced into the bottle, the stopper quickly inserted, and the whole weighed. The head of the stopper is then weighted by wrapping a strong platinum wire round the neck, and the bottle allowed to slide, mouth downwards, into a suitable flask of about 2 litres capacity placed in an inclined position, and containing about 500 c.c. of water at 50° to 60°. The flask is next placed in an upright position and covered with a watch-glass. It is advisable to bind the stopper to the bottle with thin platinum wire, to prevent its falling out.

With suitable weighting the bottle takes up an oblique position in the water, the head being directed downwards, which is the best position for the subsequent operation. At first the warmth of the water expands the air in the bottle and causes some acid to escape; later on, water is drawn in and dilutes the contents of the bottle without producing too violent a reaction. The dilution may be hastened by cooling the flask, but shaking or other violent movement must be avoided. Finally, the bottle is washed inside and out with water, the cooled solution made up to 1 litre, and 100 c.c. titrated with $N/5$ alkali as above.

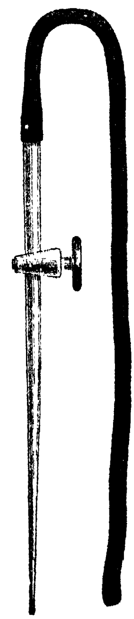
FIG. 200.

A very convenient apparatus for weighing fuming sulphuric acid or melted anhydride is the glass tap-tube recommended by Winkler (Fig. 200).

The conically narrowed portion ending in a capillary must be

absolutely uniform, and the tap, which may not be greased, should fit perfectly. The longer portion of the tube is one-half, or at most two-thirds, filled by suction with the acid to be examined, the tap closed, and the tube then inverted so that the acid runs down to the tap. The end of the tube is carefully cleaned with paper, and the tube and contents weighed in a horizontal position. No alteration in weight during weighing need be feared. The tube is then placed with the point downwards in a beaker containing water and the acid allowed to enter the water very gradually, the rate of the flow being best regulated by means of a screw clip. In the case of very strong acids or of pure anhydride which will remain liquid for a considerable time, dilution is effected by allowing the acid to escape on to a layer of coarsely powdered, crystallised, and perfectly neutral Glauber's salt. In this way dilution takes place quietly and without danger, on account of the water of crystallisation present in the salt. Finally, a few drops of water are allowed to enter the weighing-tube from above, and after standing for a short time the tube is thoroughly washed out. The Glauber's salt is dissolved in water, the solution made up to a known volume, and an aliquot portion titrated. This plan does not, however, give quite accurate results, as the colour change of the indicator (methyl orange) is less sharp in presence of the Glauber's salt.

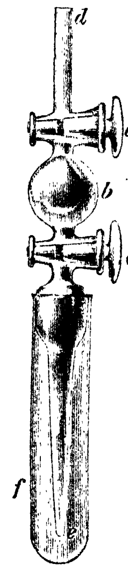

FIG. 201.

The most convenient form of weighing apparatus, not only for oleum but also for other liquids, such as fuming acids of all kinds, ammonia, etc., which must be weighed out of contact with air, is the bulb-tap pipette designed by Lunge and Rey (Fig. 201).

The taps *a* and *c* must fit perfectly without grease. To fill the pipette the tap *c* is closed, *a* opened, and, whilst applying suction at *d*, closed so that a partial vacuum is obtained in the bulb *b*. The point *e* of the tube is then placed in the acid, and *c* opened, whereby the acid rises in the pipette. Care must be taken that it does not reach the tap *c*; all vapours are retained in *b*. The tap *c* is then closed, the end of the tube *e* cleaned, and after returning the pipette to the protecting tube *f*, the whole is weighed. In the case of strongly fuming nitric acid and similar liquids a drop of the liquid may escape from the point *e* during the weighing; in such cases it is advisable to place a little water in the tube *f*, taking care, however, not to insert the empty pipette before the final weighing, lest its point become wetted. The pipette is then removed from *f*, the point *e* dipped into water, and the contents allowed to escape gradually by opening the tap *c*; a

little water is admitted to *b* through *d* and *a*, and the whole finally washed after allowing to stand for some time. If only 0·5 to 1 g. of acid has been weighed off, the whole of the resulting solution is titrated, the result obtained being more accurate in this case than by diluting to a large volume and only titrating a portion. For larger quantities of acid the solution must be diluted to a measured volume and an aliquot part titrated.

The strongest oleum (over 70 per cent.) cannot be run into water directly without undergoing loss. Such acid is weighed in the bulb-tubes described above, both capillary ends fused, and the bulb placed in a flask containing a fairly large volume of water. The flask is then closed with a glass stopper, the bulb broken by shaking the flask, and after standing for some time the whole is titrated.

For other apparatus for the weighing off and dilution of samples of oleum, with diagrams illustrating their mode of action, see Finch,[1] Vernon,[2] and Berl.[3]

Rosenlecher[4] has described the method employed at Freiberg for checking the process in the works. Weighing-tubes of the dimensions

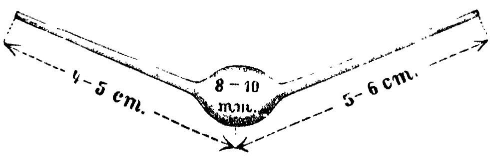

FIG. 202.

shown in Fig. 202 are made from glass tubing of 5 to 6 mm. diameter; a number of them are prepared at one time. The ends of the capillaries are narrowed to ½ mm., and for strong oleum or anhydride to ¼ mm. The bulbs are filled by suction applied by the mouth through a capillary rubber tube fixed to the shorter capillary, a test-tube filled with soda crystals being interposed when necessary. Suction is applied until the liquid begins to rise in the bulb, and is stopped before the heavy anhydride vapours reach the shorter limb. The bulb is then turned so that the limbs point upwards, and the bulk of the liquid brought into the bulb by gentle tapping. Each bulb is carefully wiped with filter paper and supported opposite a corresponding number in a notched cardboard box. In weighing, the bulb is placed on a platinum crucible (p. 461), or held in a suitable brass wire support. If the above dimensions of the capillaries are adhered to, there is no danger of moisture being absorbed or of loss by evaporation, even in the case of pure anhydride. Care must, however, be taken not to warm the bulbs in handling, either before or after weighing. To bring the

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 625.
[2] *J. Chem. Soc.*, 1910, **98** (ii.), 803.
[3] *Chem. Zeit.*, 1910, **34**, 428.
[4] *Z. anal. Chem.*, 1898, **37**, 209.

acid into solution the bulb is placed in a bottle containing the indicator and 20 to 30 c.c. of water, at the temperature of the room. The previously wetted glass stopper of the bottle is then inserted, the bottle held in a horizontal position (the colour of the indicator should remain unchanged up to this time), the stopper securely fixed, and the bottle well shaken until the tube has been completely shattered and all white vapours have disappeared. The solution is then titrated in the bottle itself. The differences in the results obtained seldom exceed 0·15 per cent. even with rapid working. (This statement apparently relates to the total acidity and not to the free anhydride.)

Dobriner and Schranz[1] dissolve 6 to 8 g. of the oleum contained in a sealed tube by breaking the tube in a stoppered litre flask containing about 150 c.c. of water, and adding a weighed quantity of chemically pure dry sodium carbonate, so that only 3 to 4 c.c. of normal solution are required for titrating back. By this means errors in the standard solution, and in the burette, etc., are reduced to a minimum.

As already stated (p. 461), a deduction must always be made for sulphurous acid, which is seldom absent from commercial oleum. The sulphurous acid is usually determined by titration with iodine and the quantity found deducted from the total acidity. Lunge[2] has pointed out that an error may easily occur in the latter titration, unless due attention be paid to the indicator employed and the stage at which the change of colour takes place; great differences exist between the various indicators in this respect. Thus with phenolphthalein the change occurs when 1 mol. SO_2 has combined with 2 mol. NaOH, that is, when Na_2SO_3 has been formed; with methyl orange, on the other hand, the change takes place when only 1 mol. NaOH has been added for 1 mol. SO_2, that is, as soon as $NaHSO_3$ has been produced. Litmus cannot be employed, since the results obtained are quite indefinite, lying between the limits given above, nor is phenolphthalein a good indicator in this case, owing to the unavoidable presence of carbonate in the sodium hydroxide solution. Ammonia is unsuitable for the titration. Methyl orange should therefore be used, bearing in mind that 1 c.c. normal sodium hydroxide solution (0·04006 g. NaOH) is neutralised by $\frac{1}{2}$ mol. SO_3 (0·04003 g. SO_3), but by a full molecule of SO_2 (0·06405 g. SO_2). Consequently for each 1 c.c. $N/10$ iodine solution required for the titration of the latter only 0·05 c.c. normal alkali solution must be allowed, and not the equivalent ratio 0·1 c.c. If this point be neglected very considerable error may result, since everything other than SO_2 and SO_3 is assumed to be water; thus an incorrect allowance for sulphur dioxide will not only show too little

[1] *Z. angew. Chem.*, 1896, **9**, 453.
[2] *Ibid.*, 1895, **8**, 22.

trioxide, but also a corresponding quantity of water in excess of the real value, and since the latter has to be credited with its corresponding amount of SO_3 (= 4·443 times the quantity of water), the percentage of free trioxide may come out very much too low. In an actual case the incorrect allowance for SO_2 led to an error of 8¼ per cent. in the free SO_3. This is, however, an extreme instance.

If the proportion of free trioxide is calculated by means of the table (p. 467), instead of by multiplying the water by 4·443, due allowance must similarly be made for the content of sulphur dioxide. Thus, taking the actual case just referred to, analysis proved the acid to contain 95·21 per cent. SO_3, 2·43 per cent. SO_2, and 2·36 per cent. H_2O. In using the table the SO_2 must be left out of account, that is, the SO_3 and H_2O are the only factors to be considered. It will not do merely to take from the table the value corresponding to a total percentage of 95·21 SO_3; this would only give 73·95 per cent. free SO_3, an even more incorrect result than the above. The correct procedure is to add the 2·36 parts H_2O to the 95·21 parts SO_3, giving in all 97·57 parts of acid and water with a percentage content of 97·58 SO_3. According to the table, it is found by interpolation that such acid corresponds to 86·80 per cent. free SO_3 and 12·20 per cent. H_2SO_4. This 86·80 per cent. must then be recalculated to the original acid, and so allow for the contained SO_2, giving $\frac{97 \cdot 57 \times 86 \cdot 80}{100} = 84 \cdot 69$ per cent. free SO_3 as the final value. The result obtained thus involves considerably more calculation than multiplying the percentage of water by its equivalent of sulphur trioxide; it is only fair to state, however, that this example does not lend itself particularly well to the table, which is drawn up for mixtures of anhydride and water only.

In the foregoing instance, as in all methods hitherto published for determining the strength of oleum, everything other than SO_2 and SO_3 is regarded as water. It is, however, advisable to estimate the *fixed impurities* by evaporation, since otherwise their weight multiplied by 4·443 is erroneously deducted from the free SO_3.

The results of the titration are first calculated to percentage o total SO_3 (combined and uncombined with water), each 1 c.c. normal sodium hydroxide solution corresponding to 0·04003 g. SO_3; the ratio between free SO_3 and the H_2SO_4 present may then be taken from the following table drawn up by Knietsch.[1] Or the general formula,

$$SO_3 = S - 4.443\,(100 - S),$$

may be employed, in which SO_3 stands for the free sulphur trioxide and S for the total SO_3, as found by titration.

[1] *Ber.*, 1901, **34**, 4114.

Table for finding the Percentage of Free SO_3 in Oleum from the Total SO_3 as determined by Analysis. Knietsch.

SO_3		SO_3		SO_3		SO_3		SO_3		SO_3	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81·63	0·0	84·7	16·7	87·8	33·6	90·9	50·5	94·0	67·3	97·0	83·7
81·7	0·4	84·8	17·2	87·9	34·1	91·0	51·0	94·1	67·9	97·1	84·2
81·8	0·9	84·9	17·8	88·0	34·7	91·1	51·6	94·2	68·4	97·2	84·8
81·9	1·5	85·0	18·3	88·1	35·2	91·2	52·1	94·3	69·0	97·3	85·3
82·0	2·0	85·1	18·9	88·2	35·8	91·3	52·6	94·4	69·5	97·4	85·8
82·1	2·6	85·2	19·4	88·3	36·3	91·4	53·2	94·5	70·1	97·5	86·4
82·2	3·1	85·3	20·0	88·4	36·8	91·5	53·7	94·6	70·6	97·6	86·9
82·3	3·6	85·4	20·5	88·5	37·4	91·6	54·3	94·7	71·2	97·7	87·5
82·4	4·2	85·5	21·0	88·6	37·9	91·7	54·8	94·8	71·7	97·8	88·0
82·5	4·7	85·6	21·6	88·7	38·5	91·8	55·4	94·9	72·2	97·9	88·6
82·6	5·3	85·7	22·2	88·8	39·0	91·9	55·9	95·0	72·8	98·0	89·1
82·7	5·8	85·8	22·7	88·9	39·6	92·0	56·4	95·1	73·3	98·1	89·7
82·8	6·4	85·9	23·2	89·0	40·1	92·1	57·0	95·2	73·9	98·2	90·2
82·9	6·9	86·0	23·8	89·1	40·6	92·2	57·5	95·3	74·4	98·3	90·7
83·0	7·5	86·1	24·3	89·2	41·2	92·3	58·1	95·4	75·0	98·4	91·3
83·1	8·0	86·2	24·9	89·3	41·7	92·4	58·6	95·5	75·5	98·5	91·8
83·2	8·5	86·3	25·4	89·4	42·3	92·5	59·2	95·6	76·1	98·6	92·4
83·3	9·1	86·4	26·0	89·5	42·8	92·6	59·7	95·7	76·6	98·7	92·9
83·4	9·6	86·5	26·5	89·6	43·4	92·7	60·3	95·8	77·1	98·8	93·5
83·5	10·2	86·6	27·0	89·7	43·9	92·8	60·8	95·9	77·7	98·9	94·0
83·6	10·7	86·7	27·6	89·8	44·5	92·9	61·3	96·0	78·3	99·0	94·6
83·7	11·3	86·8	28·1	89·9	45·0	93·0	61·9	96·1	78·8	99·1	95·1
83·8	11·8	86·9	28·7	90·0	45·6	93·1	62·4	96·2	79·3	99·2	95·6
83·9	12·3	87·0	29·2	90·1	46·1	93·2	63·0	96·3	79·9	99·3	96·2
84·0	12·9	87·1	29·8	90·2	46·6	93·3	63·5	96·4	80·4	99·4	96·7
84·1	13·4	87·2	30·3	90·3	47·2	93·4	64·1	96·5	81·0	99·5	97·3
84·2	14·0	87·3	30·9	90·4	47·7	93·5	64·6	96·6	81·5	99·6	97·8
84·3	14·5	87·4	31·4	90·5	48·3	93·6	65·2	96·7	82·0	99·7	98·4
84·4	15·1	87·5	31·9	90·6	48·8	93·7	65·7	96·8	82·6	99·8	98·9
84·5	15·6	87·6	32·5	90·7	49·4	93·8	66·2	96·9	83·1	99·9	99·5
84·6	16·2	87·7	33·0	90·8	49·9	93·9	66·8	...	...	...	...

Grünhut[1] gives the following table (p. 468), which allows the percentage to be read directly to the hundredth part. The left-hand portion shows the amount of trioxide corresponding to the total percentage of H_2SO_4 as found. For 106 per cent. H_2SO_4, for example, the point of intersection of the vertical column 10 and the horizontal row 6 gives the desired percentage 26·657. The right-hand portion contains the values for the decimal places. The first decimal is found in the vertical column marked by the asterisk, and the horizontal line lying to the right is then followed until the column having the second decimal place for its heading is reached. Thus for 0·78 per cent. H_2SO the value is 3·465. The desired result is then obtained by adding the percentages found for the whole numbers and for the decimals. Thus, had the titration given 106·78 per cent. H_2SO_4, the percentage of trioxide present in the oleum would be $26·657+3·465=30·12$ per cent. The

[1] *Z. anal. Chem.*, 1899, 38, 167.

corrections for SO_2 and fixed residue must, of course, be made as described (p. 466), before making use of these tables.

Table for finding the Percentage of SO_3 in Oleum from the Total Acidity calculated as H_2SO_4. Grünhut.

Whole Numbers.			*	Hundredth Parts.									
10	11	12		0	1	2	3	4	5	6	7	8	9
0	44·428	88·857	0	0	0·044	0·089	0·133	0·178	0·222	0·267	0·311	0·355	0·400
4·443	48·871	93·300	1	0·444	0·489	0·533	0·578	0·622	0·666	0·711	0·755	0·800	0·844
8·886	53·314	97·743	2	0·889	0·933	0·977	1·022	1·066	1·111	1·155	1·200	1·241	1·288
13·329	57·757	...	3	1·333	1·377	1·422	1·466	1·511	1·555	1·599	1·644	1·688	1·733
17·771	62·200	...	4	1·777	1·822	1·866	1·910	1·955	1·999	2·044	2·088	2·133	2·177
22·214	66·643	...	5	2·221	2·266	2·310	2·355	2·399	2·444	2·488	2·532	2·577	2·621
26·657	71·085	...	6	2·666	2·710	2·755	2·799	2·843	2·888	2·932	2·977	3·021	3·066
31·100	75·528	...	7	3·110	3·154	3·199	3·243	3·288	3·332	3·377	3·421	3·465	3·510
35·543	79·971	...	8	3·554	3·599	3·643	3·688	3·732	3·776	3·821	3·865	3·909	3·954
39·986	84·414	...	9	3·999	4·043	4·087	4·132	4·176	4·221	4·265	4·310	4·354	4·398

Setlik[1] has described a simple and rapid method for the estimation of fuming sulphuric acid, which depends on the known property of oleum to fume in the air until all anhydride present has been converted to monohydrate. The analysis is carried out as follows. At least 50 g., or preferably 100 g., to simplify the calculation, of the sample is weighed off on an ordinary balance to within 0·1 g., into a long-necked flask of from 130 to 200 c.c. capacity, and distilled water dropped in very slowly from a tap burette graduated in $\frac{1}{10}$ c.c. and provided with a fine exit-tube.

As the reaction is very violent, means must be provided for keeping the flask well cooled. At the start the drops of water falling into the oleum fizz violently and give rise to dense fumes; as the titration proceeds, the reaction becomes less violent and the fumes less dense. Towards the end of the titration the shaking must be continued sufficiently long, after the addition of each drop, to allow the sulphuric acid fumes to be completely absorbed; this is necessary to permit of proper observation. The reaction is finished when no further fumes form on the surface of the acid and a drop of water falling in the centre dissolves quietly.

The calculation of the analysis is very simple: 9 c.c. H_2O saturate 40 g. SO_3, or 100 c.c. H_2O correspond to 444 g. SO_3. If, for example, 100 c.c. of oleum have been taken, and 6 c.c. of water required, the sample contains 26·64 per cent. free SO_3.

It is advisable to have an approximate knowledge of the strength of

[1] *Chem. Zeit.*, 1889, 13, 1670.

the oleum before making the analysis, since an oleum containing over 35 per cent. SO_3 does not lend itself to direct titration, owing to the violence of the reaction. In such cases the sample should be reduced to from 30 to 35 per cent. oleum by addition of sulphuric acid monohydrate. The monohydrate used for this purpose must, of course, have been carefully prepared, and should be stored in well-stoppered bottles. Setlik recommends the method for works use, and claims that with a little practice the test is quickly carried out, and is as accurate as titration with alkali, especially if the acid be contaminated with sulphurous acid, arsenious acid, sulphate of iron, or other impurity.

Parker[1] worked out the same method independently, and confirms Setlik's claims as to the constancy and accuracy of the results it yields He considers it to be preferable to titration with alkali, and suitable for commercial determinations as well as for works control.

Rabe's method[2] is somewhat similar in principle, but sulphuric acid of known strength (say 95 per cent.) is employed for titrating in place of the water. This substitution only complicates the method and renders the results less exact.[3]

Both methods are intended for works use only, and not for the analysis of acids intended for sale.

H. Howard[4] assays oleum by making use of the heat-evolution on admixture with sulphuric acid. He weighs 100 grms. of oleum into a Dewar tube, takes its temperature (a), adds 100 grms. of 92 per cent. sulphuric acid, of which the temperature has also been taken (b), and ascertains the temperature of the mixture (c). The rise of temperature, $c - \frac{a+b}{2}$, is determined by, and corresponds to, the composition of the oleum. To avoid calculations involving the heat-capacity of the container, a series of determinations with acids of known composition is made, and a table formed connecting rise of temperature with percentage of H_2SO_4 or of free SO_3. The process is very rapid and the results are accurate (1 per cent. difference in free SO corresponds with about 6° difference in rise of temperature).

CHLOROSULPHONIC ACID

Chlorosulphonic acid, SO_3HCl, has a specific gravity of 1·784 at 0° C., and boils at 153° C. It is decomposed by water with violence, forming sulphuric and hydrochloric acids. From the method of its preparation, it is liable to contain an excess either of hydrochloric acid or of sulphuric acid and sulphur trioxide.

[1] *J. Soc. Chem. Ind.*, 1917, **36**, 692.

[2] *Chem. Zeit.*, 1901, **25**, 345.

[3] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. i., p. 367.

[4] *J. Soc. Chem. Ind.*, 1910, **29**, 3.

For its analysis, 3 or 4 grms. is weighed off in a small sealed bulb, which is then placed in a strong bottle or flask containing 25 to 50 c.c. of water; the bottle is stoppered, wrapped in a cloth, and violently shaken so as to break the bulb and mix its contents with the water. When the action is over, the acid solution is titrated by $N/1$ sodium hydroxide with phenolphthalein or methyl red. (It is convenient to mix with the water, before introducing the bulb, a measured quantity, insufficient for neutralisation, of the normal alkali, and finish the titration after the reaction.)

The neutralised liquid is now made up to a definite bulk, and the chlorine determined in an aliquot portion by $N/10$ silver nitrate solution with potassium chromate as indicator.

The total acid from the first titration is calculated as SO_3, and the chlorine from the second as HCl (per 100 grms.). The equivalent in SO_3 of this HCl, subtracted from the total acid, gives the total SO_3. This and the HCl together, subtracted from 100, give the water, present, of course, not as water but as H_2SO_4; and the equivalent in SO_3 of this water, subtracted from the total SO_3, gives the SO_3 present as chlorosulphonic acid and (if any) free SO_3. This quantity of SO_3, and the HCl found, are separately calculated into SO_3HCl. If the former result be the greater, there is no free hydrochloric acid, and the difference between the two results, calculated from SO_3HCl to SO_3, gives the free sulphur trioxide. If the latter result be the greater, there is no free sulphur trioxide, and the difference, calculated from SO_3HCl to HCl, gives the free hydrochloric acid.

NITRIC ACID MANUFACTURE

Chili saltpetre is the only raw material employed in this industry which is dealt with in this section. The testing of sulphuric acid and of the various waste acids from the manufacture of nitrobenzene, nitroglycerin, pyroxylin, etc., which are frequently used in the nitric acid industry, is described in other sections (pp. 416 *et seq.*; 497 *et seq.*).

CHILI SALTPETRE

Chili saltpetre should contain at least 95 per cent., and the better qualities 96 to 98 per cent. of sodium nitrate. In addition to this there may occur potassium nitrate,[1] occasionally up to 9 per cent., sodium chloride, sodium sulphate, sodium iodate, sodium perchlorate, and insoluble matter; also, in exceptional instances, sodium carbonate, magnesium sulphate, and salts of the heavy metals.

[1] *Cf.* Lunge, *Chem. Ind.*, 1886, **9**, 269; Hagen, *Chem. Zeit.*, 1891, **15**, 1528; and, *Z. angew. Chem.*, 1893, **6**, 495 and 698.

Of these substances the following are usually only tested for qualitatively.

Potassium, detected by platinic chloride or sodium cobaltinitrite.

Iodates. According to Beckurts,[1] the solution is acidified with nitric acid and potassium iodide-starch solution added; the method will detect $\frac{1}{100}$ mg. of iodic acid in 1 g. nitre. Or the iodic acid may be reduced by zinc and the iodine liberated by heating with strong sulphuric acid, the solution diluted and shaken with carbon bisulphide, which will extract any iodine present, giving a rose-red solution.

Bromine, under similar conditions, colours the carbon bisulphide yellow to reddish yellow.

Sodium perchlorate, the presence of which was first recognised by Beckurts,[2] and has since been repeatedly confirmed, is, according to van Breukeleeven,[3] most easily detected by a micro-chemical test. This is carried out by adding a little rubidium chloride to a few drops of a concentrated filtered solution of the saltpetre placed on a glass slide. Permanganate is added to the solution to the production of a wine-red colour, and the solution evaporated till single crystals form, when the slide is placed under the microscope and examined to see whether, in addition to the colourless crystals of sodium nitrate, the reddish-violet crystals of rubidium perchlorate are also present. H. Fresenius and Bayerlein [4] recommend this method.

Commercial Assay of Saltpetre

In commercial dealings in Chili saltpetre an indirect method of valuation has been generally employed until quite recently, and is still used to a considerable extent for the large shipments to England.

According to this method only the percentages of moisture, sodium chloride, sodium sulphate, and matter insoluble in water are determined, the sum of these being called the *refraction*; it is assumed that all the rest is actual nitrate. This method [5] cannot in any way be looked upon as accurate, and may lead to considerable error.

For example, the method quite overlooks any potassium nitrate which may be present (*cf.* p. 470), and which, even in refined nitre, may reach several per cent. Since the nitrate is employed for the manufacture of nitric acid, explosives, etc., the higher nitrogen content of sodium nitrate as compared with that of the potassium compound is the chief consideration, and it cannot be a matter of indifference to the manufacturer whether he, for instance, receives 9 per cent. potassium nitrate in place of 9 per cent. sodium nitrate, or whether a lot which,

[1] *Pharm. Centr.*, 1886, 233.
[2] *Fischer's Jahresber.*, 1886, 305.
[3] *Chem. Centr.*, 1898, I., 960.
[4] *Z. anal. Chem.*, 1898, 37, 501.
[5] *Cf.* Alberti and Hempel, *Z. angew. Chem.*, 1892, 5, 101.

according to the analytical results shows 96 to 97 per cent. of sodium nitrate, on testing with the nitrometer is found to contain only 94 to 95 per cent. In addition, the "refraction method" also includes as nitrate any perchlorate which is present.

COMPLETE ANALYSIS, WITH EXCEPTION OF THE DETERMINATION OF NITRATE AND PERCHLORATE

Moisture.—0·8 g. of the well-mixed and coarsely powdered sample is weighed into a platinum crucible, and cautiously heated over a small flame, so as just to fuse the nitrate; with a little practice it is easy to hit off this point exactly without it being necessary to observe the temperature. The crucible and contents are then allowed to cool in a desiccator and weighed; the heating is repeated at the same temperature, to make certain that constant weight has been reached.

Or 10 g. of the nitrate is dried in the air-bath at 130°, until the weight is constant.

Insoluble Matter.—Fifty g. of the saltpetre is weighed into a beaker on a balance turning to 0·05 g. The sample is dissolved in water and filtered through a filter paper previously tared against a similar paper; the washed residue and the tare are then dried together and weighed.

Should the insoluble residue appear to contain appreciable quantities of organic matter, the latter is determined approximately by igniting the filter paper and insoluble residue. The previous drying of the residue is, in this case, preferably done at a higher temperature, say 120° to 130°, since otherwise there is always a small difference between the weight obtained by drying at 100° and that got by ignition, even in samples perfectly free from organic matter.

Chlorine, Sulphuric acid, Calcium, Magnesium, and Sodium carbonate.—Five g. of the sample is placed in a filter paper standing over a 500 c.c. flask, and dissolved by addition of boiling water; any sand remaining on the filter after washing is complete, is ignited and weighed. The filtrate when cold is made up to 500 c.c., and of this solution 50 c.c. is taken for the determination of chlorine by titration or precipitation with silver nitrate (p. 73), the result being calculated to sodium chloride. A further 50 c.c. is heated to boiling, and precipitated with barium chloride, the resulting barium sulphate filtered off, weighed, and calculated to calcium sulphate. To estimate the calcium and magnesium, 20 g. of saltpetre is dissolved in 1000 c.c. of boiling water, and the calcium estimated by the addition of ammonium oxalate to 500 c.c. of this solution, the magnesium in the filtrate from the calcium precipitation by addition of ammonium phosphate. The sodium carbonate is obtained by treating 100 c.c. of this solution

with sulphuric acid, evaporating to dryness, and igniting until the weight of the residue is constant. The sodium carbonate is calculated from the weight of sulphate so obtained, after making allowance for the calcium and magnesium sulphates present. Any potassium present must also be allowed for. The sodium carbonate is often obtained by difference.

Potassium.—Potassium was formerly estimated indirectly by converting the bases into sulphates, but the method leads to very uncertain results when, as in this case, one of the constituents is present in only very small proportion.

A much more exact method consists in repeated evaporation of the saltpetre with strong hydrochloric acid and precipitation with platinic chloride, as described in the section on "Potassium Salts" (Vol. II.).

The potassium is calculated to potassium nitrate, one hundred parts of which are equivalent to 84·09 parts $NaNO_3$.

THE ESTIMATION OF NITRATE

Numerous methods, of very unequal value, have been proposed for the estimation of nitric acid in saltpetre. These are grouped together in the following list as arranged by Böckmann, with several additions of recent date; it is essentially a summary, and does not make any pretence to be complete.

I. Methods depending on Reduction to Nitric Oxide.

A. *By measurement of nitric oxide.* 1. Lunge's nitrometric method (p. 78).

2. The method of Schlösing-Grandeau [1] as improved by P. Wagner [2] (p. 482).

B. *Volumetric determination of the nitric acid obtained on oxidising nitric oxide with hydrogen peroxide.* Wilfahrth's method.[3]

C. *Reduction by ferrous salts and subsequent titration with permanganate solution.* Method of Pelouze and Fresenius.

Method of Russo and Sensi.[4]

II. Reduction to Ammonia in Alkaline Solution.

There are many modifications of this method, of which the following may be mentioned :—

1. Stutzer's method.[5] Reduction by sodium hydroxide and aluminium

[1] *Agrikulturchem. Analyse*, p. 31.
[2] *Chem. Zeit.*, 1883, 7, 1710; 1884, 8, 475.
[3] *Z. anal. Chem.*, 1888, 27, 411.
[4] *Gazz. Chim. Ital.*, 1914, 44, 9. See also J. E. Clennell, *Eng. and Min. J.*, 1918, 106, 660.
[5] *Z. angew. Chem.*, 1890, 3, 695.

wire. Aluminium prepared by the old method of manufacture is the only kind suitable, and this has ceased to be an article of commerce.

2. Sievert's method.[1] Reduction with zinc dust and iron powder in alcoholic potassium hydroxide solution.

3. Arnd's method.[2]

III. Reduction to Ammonia in Acid Solution.

1. Ulsch's method.[3] Reduction by ferrum redactum, and dilute sulphuric acid, with subsequent distillation after rendering alkaline with sodium hydroxide solution. The method is described on p. 476.

2. Schmitt's method.[4] Reduction by a mixture of zinc and iron dust in acetic acid solution.

3. Hildesheimer's modification[5] of Jodlbauer's method. Reduction with phenolsulphuric acid, zinc dust, and mercury.

4. Förster's method.[6] Reduction with sulphosalicylic acid, sodium thiosulphate, and mercury.

5. Ulsch's electrolytic method.[7]

6. Ingham's electrolytic method.[8]

IV. Reduction to Nitrous Acid.

Gantter's method.[9] Reduction by phosphorous acid, and measurement of the nitrogen evolved on heating the resulting ammonium nitrite.

V. Estimation of Nitric Acid by means of the Hydrogen Deficit.

Ulsch's method.[10] A measured quantity of sulphuric acid is allowed to act on strongly coppered iron alone and, separately, upon the couple together with the nitrate solution; the hydrogen evolved in the two cases is measured in the nitrometer and the volumes compared.

VI. Decomposition with Hydrochloric Acid.

1. Förster's method.[11] Two to 3 g. of the saltpetre, dried at 150°, is evaporated with 25 c.c. of 19 per cent. hydrochloric acid three times successively in a roomy porcelain crucible on the water-bath, and the resulting chloride dried at 150° and weighed. The nitrogen equals the loss in weight of the dried saltpetre $\times$ 0·5274.

[1] *Cf.* Fricke, *Z. angew. Chem.*, 1891, 4, 240.
[2] *Z. angew. Chem.*, 1917, **30**, 169.
[3] *Chem. Centr.*, 1890, II., 926; *Z. angew. Chem.*, 1891, 4, 241.
[4] *Chem. Zeit.*, 1890, 14, 1410; *Z. angew. Chem.*, 1891, 4, 240.
[5] Sullwald, *Chem. Zeit.*, 1890, 14, 1674.
[6] *Chem. Zeit.*, 1889, 13, 229; 1890, 14, 1674.
[7] *Z. Elektrochem.*, 1897, 3, 546.
[8] *J. Amer. Chem. Soc.*, 1904, **26**, 1241.
[9] *Z. anal. Chem.*, 1895, **34**, 25.
[10] *Ibid.*, 1891, **30**, 175.
[11] *Chem. Zeit.*, 1890, 14, 509.

2. Gowan's method.[1] Decomposition with hydrochloric acid and absorption of the resulting nitrosyl chloride and chlorine in potassium iodide:—

$$HNO_3 + 3HCl = Cl_2 + NOCl + 2H_2O. \qquad (1\ HNO_3 = 3Cl).$$

3. Bohlig's method.[2] Decomposition with sulphuric and hydrochloric acids, absorption of the liberated chlorine in potassium ferrocyanide, and subsequent titration with permanganate.

4. Bensemann's method.[3]

VII. Ignition Methods.

1. Chromate method } These methods are described on p. 483.
2. Silica method }

VIII. Combustion Methods with Soda Lime and other additions

(analogous to Will and Varrentrapp's method).

1. Arnold's method.[4] Ignition with soda lime, sodium thiosulphate, and sodium formate.

2. Houzeau's method.[5] Ignition with soda lime, sodium thiosulphate, and sodium acetate.

3. Boyer's method.[6] Ignition with soda lime, calcium oxalate, and sulphur.

IX. Precipitation by "Nitron."

Busch's method.[7] "Nitron" is the name given to the base 1:4 diphenyl 3:5 endanilodihydrotriazole; it forms a nitrate which is almost insoluble in water and which is suited for the detection and determination of nitric acid.

This summary of the better-known methods for the determination of nitric acid is included on account of the importance in industrial and agricultural chemistry of an exact determination of the nitrate in saltpetre. More detailed accounts of Ulsch's method, Lunge's nitrometric method, Wagner's improved form of the Schlösing-Grandeau method, and of the methods depending on ignition with potassium chromate and quartz respectively, are given below.

[1] *Chem. News*, 1891, **63**, 245; *Z. angew. Chem.*, 1891, **4**, 557.
[2] *Z. anal. Chem.*, 1900, **39**, 498.
[3] *Z. angew. Chem.*, 1906, **19**, 471.
[4] *Chem. Zeit.*, 1885, **9**, 715.
[5] *Ibid.*, 998.
[6] *Comptes rend.*, 1891, **113**, 503.
[7] *Ber.*, 1905, **38**, 856 and 861; *J. Soc. Chem. Ind.*, 1905, **24**, 291; Gutbier, *Z. angew. Chem.*, 1905, **18**, 494; Hes, *Z. anal. Chem.*, 1909, **48**, 81; Winkler, *Z. angew. Chem.*, 1921, **31**, 46.

Detailed Description of the Chief Methods for the Determination of the Nitrate in Saltpetre

Ulsch's Method, as modified by Böckmann.

The modifications relate to the size of the flask used for the reduction and for the subsequent distillation; to more effective air-cooling, and avoidance of other methods of cooling in the distillation; to dispensing with the special bulb-tube intended to prevent alkaline solution being carried into the distillate; to rendering a back titration unnecessary; to the construction of the absorption vessel; to the quantity of the absorbing solution, and to the strength of the sulphuric acid used for titration. Also, the weights of sample taken for analysis, of sulphuric acid for decomposition of iron powder, and of sodium hydroxide solution employed by Ulsch and Fricke are doubled. These latter changes had previously been recommended by Alberti and Hempel.[1] The essential features of Ulsch's method remain unchanged.

The following solutions are required for the determination:—1. Dilute sulphuric acid (1 : 2). 2. Sodium hydroxide solution of sp. gr. 1·25, absolutely free from nitrogen compounds. 3. $N/5$ sulphuric acid or $N/5$ hydrochloric acid prepared as described on p. 50.

Twenty g. of each of the well-mixed average samples, ground somewhat further in a porcelain mortar, is weighed out, dissolved in water, and the solutions made to 1000 c.c.; 50 c.c. (= 1·0 g. saltpetre) of each solution are then run into a round-bottomed flask of at least 1 litre capacity. The neck of the flask should be at least 10 cm. long, and of an internal diameter of 2·75 to 3 cm. One g. ferrum redactum is added to the contents of each flask, and then 20 c.c. of the diluted sulphuric acid (1 : 2); as a precaution, an ordinary glass funnel is placed in the neck of each. When the gas evolution has either ceased altogether or become very slow, it is accelerated by placing the flasks on sheets of asbestos and heating by a small flame, so that the solutions reach a quiet boil in about four minutes; boiling is then maintained for about six more minutes, at the end of which time the reduction should be complete.

The flasks are then allowed to cool slightly, in order that the subsequent addition of water shall not crack the funnels, and after the addition of about 150 c.c. of water, the solution is made alkaline by the addition of 50 c.c. of the sodium hydroxide solution prepared as above. At the same time a rapid rotary motion is given to the contents of the flask, and any syrupy material adhering to the upper walls of the flask is washed down by the aid of a wash-bottle. A pinch of zinc dust

[1] *Z. angew. Chem.*, 1891, 4, 398.

is then added to each flask, and distillation carried out as follows:—The distilling flask is placed on a sheet of asbestos card, supported on an ordinary tripod, and the neck fitted with a rubber stopper, through which a bent delivery tube passes for the escape of the gas; Lunge recommends the use of a bulb-tube. The vertical portion of this tube should have a length of 14 to 15 cm., of which 10 to 12 cm. is outside the stopper, whilst the downward portion leading to the absorption dish should be about 7 cm. long, and connected by a piece of rubber tubing about 10 cm. long to a second tube which dips into the absorption dish, care being taken that the two tubes are held flush together. This second tube is continued for about 7 cm. in the same direction as the downward bent portion of the exit-tube from the distilling flask, and is then bent at right angles and continued for a length of 50 to 60 cm., when it dips into the absorption dish. This is an ordinary earthenware dish, of about 800 c.c. capacity; it is charged with about 250 c.c. of distilled water to which about two drops of a somewhat strong solution of litmus have been added; the solution should be tinged a rather faint but distinct blue. A drop of the standard sulphuric acid is then added to the contents of the absorption vessel from a burette standing over the latter, and the solution is tested for neutrality by a piece of sensitive litmus paper (p. 44). When the solution is neutral, which may necessitate the addition of a further drop of acid, the burette is filled with acid to the zero mark and the flask heated; the contents, although thick and coloured greenish brown, owing to separation of ferrous and ferric hydroxides, distil quietly and without bumping. Four distillations can easily be carried out simultaneously, and due attention be given to the necessary additions of acid from the burette. Should the nitrate content be approximately known, as is frequently the case in works, so that 90 per cent. of the acid required for titration may be added at the start, six distillations can be attended to at the same time.

Instead of the Böckmann absorption vessel, Lunge prefers a Peligot or other similar tube, in which the gas inlet-tube does not dip into the acid used for absorption (*cf.* Fig. 203, p. 479); this avoids the risk of the acid being drawn back into the distilling flask.

As soon as the acid solution has been neutralised by the ammonia evolved in the distillation, any further ammonia that comes over is clearly indicated by blue stream lines rising from the mouth of the inlet-tube through the reddish-coloured solution. The latter soon assumes a bluish-red colour, unless fresh acid is added from the burette. Even should this take place, there will be no loss of ammonia, provided that fresh acid be added at once, always taking care to maintain the solution as nearly neutral as possible by testing with sensitive litmus paper. Towards the end of the operation, the solution in the absorption vessel becomes

appreciably warm, but no loss of ammonia need be feared on this account. Finally, when no further addition of standard acid from the burette has been necessary for several minutes, the inlet-tube is removed from the absorption vessel and, after making certain by the smell that the steam coming off is quite free from ammonia, the distillation is stopped.

With a distilling flask of the dimensions given, the surface of the liquid is about 18 cm. below the gas exit-tube, and there is consequently no danger of alkaline liquor being carried forward from the flask; in fact the water condensing on the inner end of the exit-tube always shows a neutral reaction, as may readily be proved at the end of the distillation.

Using $N/5$ sulphuric or hydrochloric acid, each 1 c.c. corresponds to 0·01700 g. $NaNO_3$, 0·02022 g. KNO_3, 0·01080 g. N_2O_5, or 0·01260 g. HNO_3. One g. pure $NaNO_3$ consequently requires 58·82 c.c. of $N/5$ acid.

Böckmann recommends the use of burettes of 100 c.c. capacity graduated to $\frac{1}{10}$ c.c.; this, however, necessitates a very inconvenient length. His proposal to use burettes of this capacity and graduated to $\frac{1}{20}$ c.c. is quite unpractical. Any great error in gauging the quantity of sulphuric acid to be added may be avoided by making the other determinations (refraction determination and potassium estimation, if necessary) prior to the nitrogen test. Should these indicate that more than 50 c.c. of acid are requisite, the full burette content of 50 c.c. may be run into the absorption vessel before beginning the distillation, the burette refilled, and the distillation started.

If the burette be read to 0·05 c.c., or preferably to 0·025 c.c., the total error will not exceed $\pm$ 0·1 per cent. of the nitrate if due precautions are taken. This degree of accuracy can, however, only be attained after considerable practice.

Vogtherr[1] recommends the apparatus described below (Fig. 203) for carrying out this test. It was primarily designed for nitrogen determinations by Kjeldahl's method, in which the digestion with sulphuric acid is carried out without the use of a fume chamber, and in the same apparatus as is used for distilling off the ammonia, and serves also for the estimation of ammonia in ammonium sulphate and for analogous determinations.

A Jena glass Kjeldahl flask is fitted above with a glass bell accurately ground in so as to be gas-tight, the bell being continued as a glass tube bent first in a slightly inclined downward direction and then vertically. The vertical portion is connected by a cork or rubber stopper with a bulb-tube the lower open end of which dips below the solution in the absorption flask. The long neck and the glass bell prevent spurting of the liquid from the reaction flask, the pear-shaped bulb prevents the

[1] *Chem. Zeit.*, 1902, 27, 988.

sucking back of the liquid used for absorption, whilst the cork or rubber connections employed are reduced to a minimum.

A drawback to this otherwise very satisfactory method lies in the fact that commercial ferrum redactum is not always sufficiently pure,

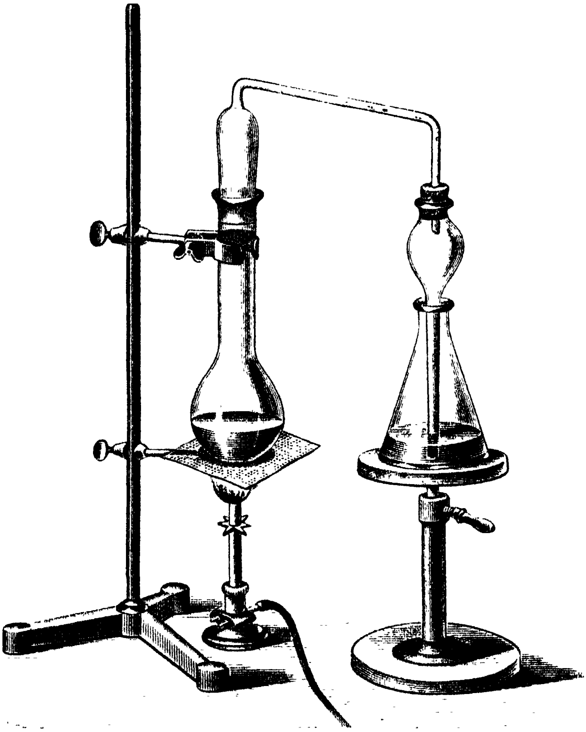

Fig. 208.

and according to Brandt,[1] errors amounting to as much as 0·8 per cent. may arise from this cause.

Allen's method[2] is as follows:—1 g. of the sample is treated with 3 g. of Devarda's alloy (containing 45 per cent. of aluminium, 50 of copper and 5 of zinc) in the presence of 25 c.c. of a 20 per cent. solution of sodium hydroxide, the ammonia produced being absorbed in standard sulphuric acid. When the violent action caused by the introduction of the alloy has subsided, the distillation is continued in a current of air, the flask being heated by immersion in boiling water; before entering the vessel containing the standard acid, the gaseous products are passed through an upwardly inclined steam-jacketed scrubber (containing glass wool) to prevent alkali "mist" from being carried

[1] *Chem. Zeit.*, 1899, **23**, 22.

[2] *Eighth Int. Cong. Appl. Chem.*, 1912, Sect. I., Orig. Comm. **1**, 19; *J. Soc. Chem. Ind.*, 1912, **31**, 921.

over. For the titration, a solution of methyl red is used as indicator; the latter being sensitive to carbon dioxide, all the water employed in the process must be boiled before use. The standardisation of the sulphuric acid in terms of sodium nitrate is effected by a procedure identical with that of the assay, pure potassium nitrate being employed for the purpose. Although not as rapid as the nitrometer method, the process is stated to be more easy of manipulation and is believed to be more accurate, the results of duplicate determinations agreeing within 0·15 per cent.

Knecht[1] dissolves 1 g. of nitrate, makes up to 100 c.c., places 10 c.c. in a copper flask (glass being too fragile), adds excess of sodium hydroxide solution, and 20 c.c. of commercial titanous sulphate or chloride. The nitrate is at once reduced to ammonia, which is distilled into a known volume of $N/10$ acid, and the excess titrated after the end of the distillation.

Other modifications of the reduction method have been devised by Beck,[2] Holtkamp,[3] Winkler,[4] Kleiber,[5] and Arnd.[6]

Lunge's Nitrometric method.—This method, which is due to W. Crum, was first rendered practically available by the introduction of Lunge's "nitrometer" (p. 78). The method depends on the fact that nitric acid, nitrous acid and their salts and esters, when brought into intimate contact with mercury and a large excess of sulphuric acid are decomposed quantitatively, so as to yield the whole of their nitrogen in the form of nitric oxide, the volume of which is measured. The reaction is:—

$$2HNO_3 + 3H_2SO_4 + 6Hg = 2NO + 3Hg_2SO_4 + 4H_2O.$$

In the analysis of saltpetre the bulb nitrometer (Fig. 26, p. 81) may be employed. It is preferable, however, to carry out the decomposition of the nitre with mercury and sulphuric acid in a special decomposition vessel, as shown in Fig. 28 (p. 82), so that the gas measurement can be made over dry mercury. The decomposition may be effected in the ordinary simple nitrometer, taking note of temperature and barometric pressure, and reducing the gas volume obtained to normal (0° and 760 mm.), but it is more convenient to employ the gas volumeter (p. 83), which allows the corrected gas volume to be read directly.

The quantity of nitre taken for the determination must be such that, under the conditions of temperature and barometric pressure obtaining at the time, not less than 100 c.c. and not more than 120 c.c. of nitric oxide are evolved. This corresponds to about 0·35 g., a quantity which has given rise to much adverse criticism of the method. So far as such criticism relates to the accuracy of the actual determination it

[1] *J. Soc. Chem. Ind.*, 1915, **34**, 126.
[2] *Z. anal. Chem.*, 1906, **45**, 671.
[3] *Z. angew. Chem.*, 1913, **26**, 600.
[4] *Ibid.*, 1913, **26**, 231; 1914, **27**, 630.
[5] *Chem. Zeit.*, 1909, **33**, 479.
[6] *Z. angew. Chem.*, 1917, **30**, 169; 1920, **33**, 296.

may be dismissed, since a gas volume of over 100 c.c. is obtained, and this volume can be read off with ease to 0·05 c.c. or even less, which means an accuracy of at least 1 in 2000. This degree of accuracy is not obtainable by any other method. There is more reason, however, in the contention that a correct average sample cannot well be obtained when so small a quantity as 0·35 g. is taken for the analysis. This objection may be overcome if, as recommended by J. Stroof, 20 g. of the nitre, dried at 110°, is thoroughly ground, and the exact average sample taken from this again dried to constant weight.

When the bulb nitrometer without a decomposing vessel is employed, the operation is carried out as follows. The well-mixed finely powdered sample, obtained as above described, is filled into a narrow, marked weighing tube, and the tube corked and weighed. When filled to the mark, the tube should contain about 0·35 g. substance. The contents are then shaken into a previously prepared "saltpetre nitrometer," that is, one of at least 130 c.c. capacity (p. 81), so that the powder falls as far as possible on to the bottom of the glass cup. During this operation the three-way cock must be in such a position that none of its passages are open either above or at the side. About half a c.c. of water is then poured in, and allowed to stand a short time until the nitre is completely or nearly dissolved, when the solution and crystals are drawn into the measuring tube by cautiously opening the tap and lowering the levelling tube; the cup is washed out with ½ or at most 1 c.c. of water, and about 15 c.c. of strong pure sulphuric acid admitted to the tube. If too much water is employed, that is, more than 1½ c.c. in all, the sulphuric acid is rendered too dilute and a persistent froth containing basic mercuric sulphate is formed, which causes difficulty in reading. The reaction is brought about by thoroughly shaking the acid solution with the mercury. The levelling tube is then placed approximately at its correct height so as to avoid any great difference of pressure and consequent error owing to leakage, and the apparatus allowed to cool for at least half an hour. The tubes are then accurately levelled, allowing one division of mercury for each six and a half divisions occupied by the acid solution in the measuring tube, and the gas volume read off. To test whether the gas is actually under atmospheric pressure, a few drops of sulphuric acid are poured into the cup, and allowed to flow into the measuring tube by cautiously opening the tap as described on p. 80.

The temperature and barometric height are read at the same time, and the gas volume reduced to 0° C. and 760 mm. pressure by means of the tables. Each 1 c.c. NO corresponds to 0·0037972 g. $NaNO_3$; the total volume x divided by the weight a taken and multiplied by 100 gives the percentage content, which is thus $= \frac{0{\cdot}37972x}{a}$.

The nitrometer must, of course, be accurately graduated, and the operator should satisfy himself that the readings are correct.

By this method it is easy to obtain results agreeing to within 0·2 per cent. Still greater accuracy may be attained with practice, certainly to at least 0·1 per cent., by using a separate decomposing vessel and transferring the gas to the measuring tube. The manipulation is much cleaner when working in this way; also several decomposing vessels may be operated at the same time and all the gas volumes read off in a single measuring tube.

If a gas volumeter be employed, the reduction tube must, of course, be set for dry gas, or if set for moist gas, the operation must be carried out as described on p. 84, most conveniently by sucking a tiny drop of water into the gas measuring tube.

Baskerville and Miller [1] have stated that mercury is attacked at ordinary temperatures by sulphuric acid of sp. gr. 1·84 with the formation of sulphur dioxide, and that this may give rise to errors in nitrometric work. Pitman [2] has shown that this objection is groundless, and this has since been admitted by the above authors; [3] they now state that such action only occurs with acid of 99 per cent. strength and not with acid of 94 to 95 per cent., such as is generally used for laboratory work.

The view that the solubility of nitric oxide in the resulting solutions may lead to appreciable error has been disproved by Lunge,[4] Nernst and Jellinek,[5] Tower,[6] and by Newfield and Marx.[7]

The Schlösing-Grandeau-Wagner Method.[8]

This method depends upon the reduction of nitric acid to nitric oxide, which is collected and measured.

The apparatus required for the determination consists of a flask of 250 to 300 c.c. capacity, closed by a double-bored rubber stopper and furnished with a tap-funnel of 15 c.c. capacity. The lower end of the funnel-tube, which is fused together so as to contract the outlet, reaches to the middle of the flask, but not to the solution. A tube, suitably bent to dip into a glass dish containing well-boiled water, passes through the second opening in the stopper and serves as the exit-tube for the liberated gas. The measuring tube, which is preferably provided with a glass tap at its upper end and graduated from the top downwards in $\frac{1}{10}$ c.c., is supported above the dish in a clamp. Forty c.c. of ferrous chloride solution, containing 400 g. per litre, and an equal

[1] *Chem. Centr.*, 1898, I., 85.
[2] *Ibid.*, 1898, I., 709.
[3] *Ibid.*, 1898, II., 89.
[4] *Ber.*, 1885, 18, 1391; 1886, 19, 111. *Chem. News*, 1886, 53, 289.
[5] *Z. anorg. Chem.*, 1906, 49, 219 and 236.
[6] *Ibid.*, 50, 382.
[7] *J. Amer. Chem. Soc.*, 1906, 28, 877.
[8] *Chem. Zeit.*, 1883, 7, 1710; 1884, 8, 475.

volume of well-boiled 10 per cent. hydrochloric acid, are introduced into the flask and the contained air expelled from the apparatus by continued boiling, care being taken that the funnel-tube always contains hydrochloric acid. When all air has been expelled the gas exit-tube is placed in position below the measuring tube and 10 c.c. of a normal saltpetre solution, containing exactly 33 g. pure sodium nitrate per litre, is introduced into the funnel-tube. The tap is then turned so as to allow this solution to flow drop by drop into the boiling ferrous chloride solution. When all but a small volume has been introduced the funnel is washed out twice with 10 per cent. hydrochloric acid, which, like the nitrate solution, is added drop by drop to the boiling solution in the flask. The operation is finished when the evolution of nitric oxide ceases. About 90 c.c. of nitric oxide should result under the foregoing conditions. The measuring tube is removed and, supported by a small dish containing water, cautiously transferred to a correspondingly tall glass cylinder filled with water. A second measuring tube is then brought into position and, without interrupting the boiling, a measured volume of a solution of the nitre to be tested is introduced and treated as above described, and so on with a third, fourth, and further tests as required. When the several tubes have attained the temperature of the cooling water the volume of nitric oxide in each is read off, after raising the tube so as to bring the water inside and outside to the same level. The content of each solution is obtained by comparing the gas volumes evolved from the sample and from the standard solution respectively. When carried out in this manner the method is very simple, and may be recommended ; it requires, however, careful manipulation.

According to Liechti and Ritter,[1] who have thoroughly investigated Schlösing's method, good results are obtained even in the presence of organic matter, for which purpose it was originally worked out ; this has, however, been disputed by R. Pfeiffer.[2]

Method by Ignition with Potassium Chromate or with Silica.

To the dried 0·8000 g. of substance used for the moisture determination (p. 472) is added approximately 3 g. of a mixture of equal parts of bichromate and neutral chromate of potassium which has been fused and finely ground when cool, and the whole heated, at first gradually and finally more strongly, till the mass melts uniformly. The loss in weight = N_2O_5. This method can only be used if the sample is quite free from alkali carbonates. An alternative method is to ignite a mixture of 2 g. of the salt with about seven times its weight of ignited silica free from carbonates, for from two to four hours at a good red heat.

[1] *Z. anal. Chem.*, 1903, 42, 1.

[2] *Ibid.*, 612.

Pauli[1] recommends this method, but Alberti and Hempel[2] together with most other authorities do not consider it sufficiently trustworthy. The method cannot be employed in the presence of perchlorate.

DETERMINATION OF PERCHLORATE AND OF CHLORATE

Sodium perchlorate is directly injurious in many of the applications of saltpetre. It occurs in practically all shipments of Chili nitre, and its presence must always be taken into account. A method for its qualitative detection has been described on p. 471.

All methods for the estimation of the perchlorate are based on a determination of the chlorine present as chloride in the sample, the conversion of perchlorate to chloride in a second portion of the material, and the determination of the total chlorine then present as chloride; the difference between the two tests represents the perchlorate.

The conversion of the perchlorate to chloride may be effected by simply heating for a sufficient length of time, whereby the oxygen of any perchlorate present is driven off.

Sjollema[3] and Freytag[4] have given detailed instructions for carrying out the estimation on this principle. To quicken the reaction and to render the complete deoxidation of the perchlorate more certain, various additions have been proposed: lead shavings (Selckmann[5]), iron filings (Hönig[6]), sodium carbonate (Förster[7]), calcium hydroxide (Blattner and Brasseur[8]).

Erck[9] proposes to decompose the chloride first by boiling with nitric acid of sp. gr. 1·4, and alcohol, and then to convert the perchlorate into chloride by ignition.

Winteler[10] has pointed out various sources of error in the earlier methods. He finds that fuming nitric acid will quantitatively reduce perchlorate to chloride at 200° in a sealed tube. Any chloric acid originally present must, however, be removed by evaporation with hydrochloric acid.

Various authorities recommend an addition of native peroxide of manganese (pyrolusite) for the better decomposition of the perchlorate. This was first proposed by Hellich.[11] Ahrens and Hett[12] heat the nitre to fusion and redness with sodium carbonate and chlorine-free manganese dioxide, to facilitate the decomposition of the perchlorate,

1 *J. Soc. Chem. Ind.*, 1897, **16**, 494.
2 *Z. angew. Chem.*, 1892, **5**, 103.
3 *Chem. Zeit.*, 1896, **20**, 1002.
4 *Chem. Centr.*, 1898, I., 1203; *Z. angew. Chem.*, 1898, **11**, 1021.
5 *Z. angew. Chem.*, 1898, **11**, 101.
6 *Chem. Zeit.*, 1903, **27**, 32.
7 *Ibid.*, 1898, **22**, 357.
8 *Ibid.*, 589.
9 *Ibid.*, 1897, **21**, 21.
10 *Ibid.*, 75.
11 *Chem. Zeit.*, 1894, **18**, 485.
12 *Chem. Centr.*, 1898, II., 558; *Z. angew. Chem.*, 1898, **11**, 1020.

treat the solution of the melt with nitric acid and potassium permanganate to permanent coloration, and determine the chloride by Volhard's method.

C. Gilbert (*Methoden zur Bestimmung des Perchlorats*, Tubingen, 1899) gives the following directions for carrying out the pyrolusite method: — Twenty-five g. of nitre is dissolved in water, made up to 250 c.c., and the chloride determined by titrating 50 c.c. of the filtered solution with silver nitrate (1 c.c. = 0·01 g. NaCl) and potassium chromate (see p. 73). A second 25 g. of the nitre, preferably after the addition of 2·5 g. of the purest powdered pyrolusite (Merck's), is heated for half an hour at 540° in an air-bath in a nickel crucible fitted with a deep concave lid, and having a capacity of 70 c.c. The aqueous solution of the melt is then made up to 250 c.c., filtered, and the chlorine again determined as above. The air-bath recommended is that designed by Lothar Meyer; it will hold from three to six crucibles, and should be fitted with a gas regulator and a Le Chatelier pyrometer or thermometer reading up to 570°. Dupré[1] proceeds in essentially the same manner, omitting the pyrolusite, but heating 20 g. of the sample for one hour at 545° in an air-bath of the type recommended by Gilbert. Instead of a pyrometer, a covered nickel crucible may be used in which is placed a platinum crucible, resting on a layer of asbestos paper, and containing about 1 g. of potassium perchlorate. By observing, after the completion of the heating, whether the residue in the platinum crucible fuses without any appreciable evolution of gas, a gauge of the temperature employed is obtained. The chloride may also be determined by Volhard's method (p. 74), or gravimetrically.

Should iodate be present, Ahrens and H. Gilbert effect the fusion with addition of sodium carbonate. Twenty g. of the dried nitrate is thoroughly moistened with 2 to 3 c.c. of a concentrated solution of sodium carbonate, 1 g. of pyrolusite added, the mixture dried and maintained in a state of fusion at a low red heat for fifteen minutes. The solution of the melt is then oxidised with potassium permanganate solution, and the chlorine determined by Volhard's method.

Sodium chlorate as well as perchlorate has been detected in Chili saltpetre, and methods for its estimation have been devised. In the examination of 107 samples of nitre, Märcker[2] found the percentage of perchlorate present to vary from 0·27 to 5·64, with a mean value of 0·94 per cent., and in addition 0·1 to 1·0 per cent. of chlorate, as determined by the method then in vogue. The presence of perchlorate is regarded as objectionable in nitre intended for agricultural purposes, and although the practical investigation into the extent of the injury it may cause has not yet been concluded, it has been suggested that the maximum quantity to be allowed should not exceed 1½ per cent.

[1] *J. Soc. Chem. Ind.*, 1902, 21, 825. [2] *Chem. Centr.*, 1898, II., 925.

Mennicke[1] estimates a mixture of chloride, chlorate, and perchlorate in the following manner. (*a*) The nitre is ignited with addition of alkali hydroxide or carbonate to convert all the chlorine compounds to chloride, which is determined. (*b*) Chloride and chlorate are estimated by gently boiling 5 g. of the nitre with 10 g. of zinc dust (free from chlorine), and 150 c.c. of 1 per cent. acetic acid for half an hour, filtering and determining the chloride. (*c*) The chloride originally present in the nitre is determined directly. This method has shown the presence of appreciable quantities of chlorate.

Blattner and Brasseur[2] treat a solution of 5 to 10 g. of the nitrate with excess of sulphurous acid, either as gas or in solution, thereby reducing only the chlorate and not the perchlorate, drive off the excess of sulphur dioxide by boiling, and saturate the warm solution with calcium carbonate. The chloride is estimated in the cold filtered solution in the ordinary manner, and the chlorine present in the sample as chlorate is obtained by deducting from this value that of the chloride originally present in the nitre. The total chlorine is determined by igniting the saltpetre with calcium hydroxide as described above, and the perchlorate arrived at by difference.

Arnould[3] has described the following method, which is employed in the French Government laboratory. The chloride originally present is precipitated by the addition of neutral silver nitrate solution and filtered off; the chlorate in the filtrate is reduced by warming this to 90°, and adding an excess of lead nitrite, prepared by simply shaking lead nitrite with water and without filtering; any cloudiness due to the nitrite is removed by the addition of a few drops of dilute nitric acid. If any opalescence persists after this treatment, chlorate is present, and the amount is estimated by comparison with similarly prepared solutions to which known quantities of chlorate have been added. For the French powder factories it is specified that the nitre must contain less than 0·01 per cent. chloride, 0·01 per cent. chlorate, and 0·1 per cent. perchlorate.

Lemaitre[4] reduces the perchlorate by fusion with sodium sulphite; this method has been improved by Tschernobojew,[5] who has shown that chlorate can be determined simultaneously.

CONTROL OF WORKING CONDITIONS

The process control in the manufacture of nitric acid consists essentially in the determination of the yield and of the quality of the nitric acid. In addition, care must be taken that no nitrogen oxides escape

[1] *Chem. Zeit. Rep.*, 1898, **22**, 117.
[2] *Ibid.*, 1900, **24**, 793.
[3] *Mémorial des poudres et salpêtres*, 1902.
[4] *Monit. Scient.*, 1904, **18**, 253; *Chem. Centr.*, 1904, **I.**, 1427.
[5] *Chem. Zeit.*, 1906, **29**, 442.

into the chimney or into the atmosphere; the tests applied are similar to those employed in the sulphuric acid industry (*cf.* p. 406).

The bisulphate drawn from the retort must also be examined; this is done in the following manner:—

1. *Free acid* is estimated by titration with normal sodium hydroxide solution. In the presence of considerable amounts of iron oxide or of alumina no indicator is added, and the titration is considered finished as soon as the first signs of a permanent flocculent precipitate appear.

2. *Nitric acid* may be determined in the nitrometer or gas volumeter as in the nitrometric method for the estimation of saltpetre. The acid sulphate is dissolved in the minimum quantity of water in the cup above the tap, and decomposed with a large excess of sulphuric acid (pp. 79 and 82). Since the quantity of nitric acid present in acid sulphate is always small, a nitrometer with a narrow measuring tube as used in the examination of acids, or with a central bulb (Fig. 27, p. 81), should be employed.

AMMONIA OXIDATION PROCESSES

In these processes ammonia is oxidised by the oxygen of atmospheric air, with the aid of a catalyst, to nitric oxide, which is then further oxidised so as to become ultimately nitric acid or a nitrate. Under certain conditions some of the ammonia may escape oxidation altogether, and some may be oxidised only so far as to produce nitrogen. For the control of the process it is necessary to know what percentage of the ammonia introduced is actually converted into oxidised nitrogen. This is ascertained by an examination of the mixture of air and ammonia introduced into the plant, and of the gases after passing the catalyst.

Methods of analysis have been described by Fox[1] and by Taylor and Davis,[2] but a considerable simplification was made by Gaillard,[3] who weighed the gases examined instead of measuring them.

The determination rests on the principle that, if all the ammonia is converted into oxides of nitrogen, the percentage by weight of nitrogen in the form of oxides in the exit gases will be equal to the percentage by weight of nitrogen in the form of ammonia in the entrance gases. If only a portion is converted, the ratio of these percentages will be a measure of the efficiency of the conversion.

Gaillard's description of his method is as follows:—Four glass bulbs (the determinations being made in duplicate) of 500 to 600 c.c. capacity, and weighing each 60 to 80 g., with gas-tight stopcocks well

[1] *J. Ind. Eng. Chem.*, 1917, 9, 737.
[2] *Ibid.*, 1917, 9, 1106.
[3] *Ibid.*, 1919, 11, 745.

greased, are evacuated to a pressure of about 2 cm. of mercury, carefully wiped outside, and weighed. A check weighing is made after a minute or so to make sure that there is no leakage. Leakage can also be detected by inverting the bulb and allowing the small quantity of water remaining from the previous test to run down into the glass tube of the stopcock, when the slightest leak will show itself by air bubbles. As soon as possible after the weighing, the bulbs are connected to short glass sampling tubes of small bore by means of tight rubber tubes; over the glass tubes are stoppers which fit tightly into the sampling holes of the converter (Fig. 204). The bulbs are now adjusted to the sampling holes, and are kept there about half a minute before the samples are taken, to bring the tubes to the same temperature as the gas. The samples are then taken as rapidly as possible, with stopcocks opened wide, to prevent moisture from condensing in the tubes. This is of special importance in the exit sample because of the water formed in the reaction. The bulbs are now disconnected from the sampling tubes, wiped, allowed to remain near the balance case for five minutes, and weighed. The tube of the bulb containing an entrance sample is immersed in distilled water and the cock opened; as much water as will is allowed to enter and the stopcock closed. The bulb is then shaken for a minute to absorb the ammonia. The tube is then applied to the mouth, the cock opened and air blown into the bulb, and the cock closed again. The contents of the bulb are then discharged into 25 c.c. of $N/10$ sulphuric acid accurately measured from a burette into a 600 c.c. beaker. The bulb is washed out three times and the washings added to the liquid in the beaker, water being introduced into the bulb each time by first sucking air out. The excess acid in the beaker is then titrated, using methyl red as an indicator.

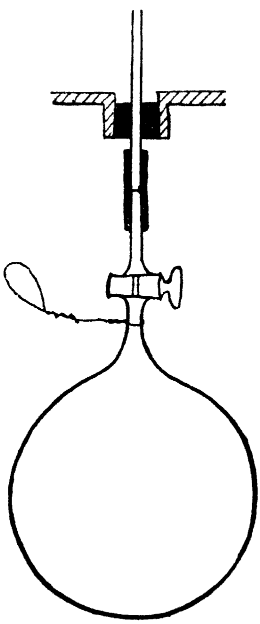

FIG. 204.

Into the bulb containing an exit sample about 100 c.c. of water is introduced, care being taken not to introduce any air. Then about 25 c.c. of oxygen is drawn in from any convenient reservoir, the bulb is shaken for a minute, and allowed to stand for at least another minute. Any vacuum remaining is then relieved by opening the stopcock to the air. The cock is then closed and the bulb shaken for five minutes. The liquid in the bulb and three subsequent washings are then transferred to a 600 c.c. beaker containing 15 c.c. of $N/10$ sodium

hydroxide diluted to about 75 c.c., and titrated, using methyl red as indicator. It is preferable to finish both titrations in the same direction, by adding in the second titration an excess of acid, and titrating back with $N/10$ alkali.

A representative calculation is given as follows:—

Entrance Samples.

	Bulb 1.	Bulb 2.
Weight of bulb and sample	63·1600	69·0565
Weight of bulb	62·5025	68·4605
Weight of sample	0·6575	0·5960
Standard acid used	21·05 c.c.	18·95 c.c.
Per cent. combined nitrogen	$\frac{21·05 \times 0·0014}{0·6575} = 4·48$	$\frac{18·95 \times 0·0014}{0·5960} = 4·45$

Exit Samples.

	Bulb 3.	Bulb 4.
Weight of bulb and sample	75·0775	67·6830
Weight of bulb	74·4865	67·0580
Weight of sample	0·5910	0·6250
Standard alkali used	17·23 c.c.	18·30 c.c.
Per cent. combined nitrogen	$\frac{17·23 \times 0·0014}{0·5910} = 4·08$	$\frac{18·30 \times 0·0014}{0·6250} = 4·10$

$$\text{Efficiency of conversion} = \frac{4·09}{4·47} = 91·6 \text{ per cent.}$$

Ammonia remaining unoxidised is usually very small in amount; but it can be estimated by colorimetric methods in the neutralised liquid from the exit samples, and the results modified accordingly.

NITRIC ACID

Pure, absolute nitric acid, HNO_3, is very difficult to prepare, and scarcely keeps any length of time, owing to the liberation of oxygen with formation of nitrogen peroxide, which latter causes the colourless acid to turn yellow or, with larger quantities of nitrogen peroxide, red. The boiling point is 86°, the specific gravity at $\frac{15°}{4°}$ slightly above 1·52.

The hydrates of nitric acid have been especially studied by Küster and Kremann.[1]

The strongest commercial acid has, when pure and almost free from nitrogen peroxide, a sp. gr. of 1·50 or slightly higher, corresponding to 94 to 95 per cent. HNO_3. It begins to boil a little above 86°, the

[1] *Z. anorg. Chem.*, 1904, **40**, 1.

boiling point rising as distillation proceeds, as more acid than water distils over, until 120·5° is reached, at which temperature an acid containing 68·9 per cent. HNO_3, and having a sp. gr. 1·42, distils over unchanged. Weaker acids have again a lower boiling point, and yield on distillation, with a continual rise in temperature, more water than acid until the boiling point 120·5° is attained, when acid of the above composition distils over.

Lunge and Rey's[1] investigations into the relationship between the specific gravity and percentage content of nitric acid solutions have led to the older tables, such as that of Kolb, being superseded. The following table is based on their researches. The specific gravity determinations made by Winteler[2] have been shown to be unreliable by Lunge,[3] by Veley and Manley,[4] and by Pützer.[5] Values agreeing with those of Lunge and Rey within, at the outside $\frac{1}{300}$ ($\frac{1}{240}$ in one case only), have been obtained by Veley and Manley,[6] who add that greater concordance is scarcely to be expected between different observers employing different methods.

An additional table (p. 493) for correcting the specific gravity obtained at higher or lower temperatures to the normal value, viz. the specific gravity of the acid at 15°, compared with water at 4° as the unit,[7] is also given.

Table of the Specific Gravity of Nitric Acid of various strengths at 15° C. referred to Water at 4° C.

Spec. Grav. at 15°/4° (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·000	0	0	0·08	0·10	0·19	0·16	0·10	0·001	0·001	0·002	0·002	0·001
1·005	0·7	1	0·85	1·00	1·89	1·61	1·03	0·008	0·010	0·019	0·016	0·010
1·010	1·4	2	1·62	1·90	3·60	3·07	1·95	0·016	0·019	0·036	0·031	0·019
1·015	2·1	3	2·39	2·80	5·30	4·52	2·87	0·024	0·028	0·053	0·045	0·029
1·020	2·7	4	3·17	3·70	7·01	5·98	3·79	0·033	0·038	0·072	0·061	0·039
1·025	3·4	5	3·94	4·60	8·71	7·43	4·72	0·040	0·047	0·089	0·076	0·048
1·030	4·1	6	4·71	5·50	10·42	8·88	5·64	0·049	0·057	0·108	0·092	0·058
1·035	4·7	7	5·47	6·38	12·08	10·30	6·54	0·057	0·066	0·125	0·107	0·068
1·040	5·4	8	6·22	7·26	13·75	11·72	7·45	0·064	0·075	0·142	0·121	0·077
1·045	6·0	9	6·97	8·13	15·40	13·13	8·34	0·073	0·085	0·161	0·137	0·087
1·050	6·7	10	7·71	8·99	17·03	14·52	9·22	0·081	0·094	0·178	0·152	0·096
1·055	7·4	11	8·13	9·84	18·64	15·89	10·09	0·089	0·104	0·197	0·168	0·107
1·060	8·0	12	9·15	10·68	20·23	17·25	10·95	0·097	0·113	0·214	0·182	0·116

[1] *Z. angew. Chem.*, 1891, 4, 165.
[2] *Chem. Zeit.*, 1905, **29**, 689 and 1009.
[3] *Ibid.*, 1905, **29**, 689 and 1072.
[4] *Ibid.*, 1905, **29**, 1270.
[5] *Ibid.*, 1905, **29**, 1221.
[6] *J. Soc. Chem. Ind.*, 1903, **22**, 1228.
[7] *Cf.* Fuchs, who has published a detailed table, *Z. angew. Chem.*, 1898, **11**, 747.

Table of the Specific Gravity of Nitric Acid, etc.—*Continued.*

Spec. Grav. at $\frac{15°}{4°}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5.	HNO_3.	Acid of 36 B.	Acid of 40° B.	Acid of 48½° B.
1·065	8·7	13	9·87	11·51	21·80	18·59	11·81	0·105	0·123	0·233	0·198	0·126
1·070	9·4	14	10·57	12·33	23·35	19·91	12·65	0·113	0·132	0·250	0·213	0·135
1·075	10·0	15	11·27	13·15	24·91	21·24	13·49	0·121	0·141	0·267	0·228	0·145
1·080	10·6	16	11·96	13·95	26·42	22·53	14·31	0·129	0·151	0·286	0·244	0·155
1·085	11·2	17	12·64	14·74	27·92	23·80	15·12	0·137	0·160	0·303	0·258	0·164
1·090	11·9	18	13·31	15·53	29·41	25·08	15·93	0·145	0·169	0·320	0·273	0·173
1·095	12·4	19	13·99	16·32	30·91	26·35	16·74	0·153	0·179	0·339	0·289	0·184
1·100	13·0	20	14·67	17·11	32·41	27·63	17·55	0·161	0·188	0·356	0·304	0·193
1·105	13·6	21	15·34	17·89	33·89	28·89	18·35	0·170	0·198	0·375	0·320	0·203
1·110	14·2	22	16·00	18·67	35·36	30·15	19·15	0·177	0·207	0·392	0·335	0·212
1·115	14·9	23	16·67	19·45	36·84	31·41	19·95	0·186	0·217	0·411	0·350	0·223
1·120	15·4	24	17·34	20·23	38·31	32·67	20·75	0·195	0·227	0·430	0·366	0·233
1·125	16·0	25	18·00	21·00	39·77	33·91	21·54	0·202	0·236	0·447	0·381	0·242
1·130	16·5	26	18·66	21·77	41·23	35·16	22·33	0·211	0·246	0·466	0·397	0·252
1·135	17·1	27	19·32	22·54	42·69	36·40	23·12	0·219	0·256	0·485	0·413	0·263
1·140	17·7	28	19·98	23·31	44·15	37·65	23·91	0·228	0·266	0·504	0·430	0·273
1·145	18·3	29	20·64	24·08	45·61	38·89	24·70	0·237	0·276	0·523	0·446	0·283
1·150	18·8	30	21·29	24·84	47·05	40·12	25·48	0·245	0·286	0·542	0·462	0·293
1·155	19·3	31	21·94	25·60	48·49	41·35	26·26	0·254	0·296	0·561	0·478	0·304
1·160	19·8	32	22·60	26·36	49·92	42·57	27·04	0·262	0·306	0·580	0·494	0·314
1·165	20·3	33	23·25	27·12	51·36	43·80	27·82	0·271	0·316	0·598	0·510	0·324
1·170	20·9	34	23·90	27·88	52·80	45·03	28·59	0·279	0·326	0·617	0·526	0·334
1·175	21·4	35	24·54	28·63	54·22	46·24	29·36	0·288	0·336	0·636	0·543	0·345
1·180	22·0	36	25·18	29·38	55·64	47·45	30·13	0·297	0·347	0·657	0·560	0·356
1·185	22·5	37	25·83	30·13	57·07	48·66	30·90	0·306	0·357	0·676	0·577	0·366
1·190	23·0	38	26·47	30·88	58·49	49·87	31·67	0·315	0·367	0·695	0·593	0·376
1·195	23·5	39	27·10	31·62	59·89	51·07	32·43	0·324	0·378	0·715	0·610	0·388
1·200	24·0	40	27·74	32·36	61·29	52·26	33·19	0·333	0·388	0·735	0·627	0·398
1·205	24·5	41	28·36	33·09	62·67	53·23	33·94	0·342	0·399	0·755	0·644	0·409
1·210	25·0	42	28·99	33·82	64·05	54·21	34·69	0·351	0·409	0·775	0·661	0·419
1·215	25·5	43	29·61	34·55	65·44	55·18	35·44	0·360	0·420	0·795	0·678	0·431
1·220	26·0	44	30·24	35·28	66·82	56·16	36·18	0·369	0·430	0·815	0·695	0·441
1·225	26·4	45	30·88	36·03	68·24	57·64	36·95	0·378	0·441	0·835	0·712	0·452
1·230	26·9	46	31·53	36·78	69·66	59·13	37·72	0·387	0·452	0·856	0·730	0·466
1·235	27·4	47	32·17	37·53	71·08	60·61	38·49	0·397	0·463	0·877	0·748	0·475
1·240	27·9	48	32·82	38·29	72·52	61·84	39·27	0·407	0·475	0·900	0·767	0·487
1·245	28·4	49	33·47	39·05	73·96	63·07	40·05	0·417	0·486	0·921	0·785	0·498
1·250	28·8	50	34·13	39·82	75·42	64·31	40·84	0·427	0·498	0·943	0·804	0·511
1·255	29·3	51	34·78	40·58	76·86	65·54	41·62	0·437	0·509	0·965	0·822	0·522
1·260	29·7	52	35·44	41·34	78·30	66·76	42·40	0·447	0·521	0·987	0·841	0·534
1·265	30·2	53	36·09	42·10	79·74	67·99	43·18	0·457	0·533	1·009	0·860	0·547
1·270	30·6	54	36·75	42·87	81·20	69·23	43·97	0·467	0·544	1·031	0·879	0·558
1·275	31·1	55	37·41	43·64	82·65	70·48	44·76	0·477	0·556	1·054	0·898	0·570
1·280	31·5	56	38·07	44·41	84·11	71·72	45·55	0·487	0·568	1·077	0·918	0·583
1·285	32·0	57	38·73	45·18	85·57	72·96	46·34	0·498	0·581	1·100	0·938	0·596
1·290	32·4	58	39·39	45·95	87·03	74·21	47·13	0·508	0·593	1·123	0·957	0·608
1·295	32·8	59	40·05	46·72	88·48	75·45	47·92	0·519	0·605	1·146	0·977	0·621
1·300	33·3	60	40·71	47·49	89·94	76·70	48·71	0·529	0·617	1·169	0·997	0·633
1·305	33·7	61	41·37	48·26	91·40	77·94	49·50	0·540	0·630	1·193	1·017	0·646
1·310	34·2	62	42·06	49·07	92·94	79·25	50·33	0·551	0·643	1·218	1·038	0·659
1·315	34·6	63	42·76	49·89	94·49	80·57	51·17	0·562	0·656	1·243	1·059	0·673
1·320	35·0	64	43·47	50·71	96·05	81·90	52·01	0·573	0·669	1·268	1·080	0·686
1·325	35·4	65	44·17	51·53	97·60	83·22	52·85	0·585	0·683	1·294	1·103	0·701
1·330	35·8	66	44·89	52·37	99·19	84·58	53·71	0·597	0·697	1·320	1·126	0·715
1·3325	36·0	66·5	45·26	52·80	100·00	85·27	54·15	0·603	0·704	1·333	1·137	0·722

Table of the Specific Gravity of Nitric Acid, etc.—*Continued.*

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (*in vacuo*).	Degrees Baumé.	Degrees Twaddell.	100 Parts by weight contain					1 Litre contains kg.				
			N_2O_5.	HNO_3	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.	N_2O_5	HNO_3.	Acid of 36° B.	Acid of 40° B.	Acid of 48½° B.
1·335	36·2	67	45·62	53·22	100·80	85·95	54·58	0·609	0·710	1·346	1·148	0·728
1·340	36·6	68	46·35	54·07	102·41	87·32	55·46	0·621	0·725	1·373	1·171	0·744
1·345	37·0	69	47·08	54·93	104·04	88·71	56·34	0·633	0·739	1·400	1·193	0·758
1·350	37·4	70	47·82	55·79	105·67	90·10	57·22	0·645	0·753	1·427	1·216	0·772
1·355	37·8	71	48·57	56·66	107·31	91·51	58·11	0·658	0·768	1·455	1·240	0·788
1·360	38·2	72	49·35	57·57	109·03	92·97	59·05	0·671	0·783	1·483	1·265	0·803
1·365	38·6	73	50·13	58·48	110·75	94·44	59·98	0·684	0·798	1·513	1·289	0·818
1·370	39·0	74	50·91	59·39	112·48	95·91	60·91	0·698	0·814	1·543	1·314	0·835
1·375	39·4	75	51·69	60·30	114·20	97·38	61·85	0·711	0·829	1·573	1·339	0·850
1·380	39·8	76	52·52	61·27	116·04	98·95	62·84	0·725	0·846	1·603	1·366	0·868
1·3833	40·0	...	53·08	61·92	117·27	100·00	63·51	0·735	0·857	1·623	1·383	0·879
1·385	40·1	77	53·35	62·24	117·88	100·51	63·84	0·739	0·862	1·633	1·392	0·884
1·390	40·5	78	54·20	63·23	119·75	102·12	64·85	0·753	0·879	1·665	1·420	0·902
1·395	40·8	79	55·07	64·25	121·68	103·76	65·90	0·768	0·896	1·697	1·447	0·919
1·400	41·2	80	55·97	65·30	123·67	105·46	66·97	0·783	0·914	1·731	1·476	0·937
1·405	41·6	81	56·92	66·40	125·75	107·24	68·10	0·800	0·933	1·767	1·507	0·957
1·410	42·0	82	57·86	67·50	127·84	109·01	69·23	0·816	0·952	1·803	1·537	0·976
1·415	42·3	83	58·83	68·63	129·98	110·84	70·39	0·832	0·971	1·839	1·568	0·996
1·420	42·7	84	59·83	69·80	132·19	112·73	71·59	0·849	0·991	1·877	1·600	1·016
1·425	43·1	85	60·84	70·98	134·43	114·63	72·80	0·867	1·011	1·915	1·633	1·037
1·430	43·4	86	61·86	72·17	136·68	116·55	74·02	0·885	1·032	1·955	1·667	1·058
1·435	43·8	87	62·91	73·39	138·99	118·52	75·27	0·903	1·053	1·995	1·701	1·080
1·440	44·1	88	64·01	74·68	141·44	120·61	76·59	0·921	1·075	2·037	1·736	1·103
1·445	44·4	89	65·13	75·98	143·90	122·71	77·93	0·941	1·098	2·080	1·773	1·126
1·450	44·8	90	66·24	77·28	146·36	124·81	79·26	0·961	1·121	2·123	1·810	1·150
1·455	45·1	91	67·38	78·60	148·86	126·94	80·62	0·981	1·144	2·167	1·848	1·173
1·460	45·4	92	68·56	79·98	151·47	129·17	82·03	1·001	1·168	2·212	1·886	1·198
1·465	45·8	93	69·79	81·42	154·20	131·49	83·51	1·023	1·193	2·259	1·927	1·224
1·470	46·1	94	71·06	82·90	157·00	133·88	85·03	1·045	1·219	2·309	1·969	1·250
1·475	46·4	95	72·39	84·45	159·94	136·39	86·62	1·068	1·246	2·360	2·012	1·278
1·480	46·8	96	73·76	86·05	162·97	138·97	88·26	1·092	1·274	2·413	2·058	1·307
1·485	47·1	97	75·18	87·70	166·09	141·63	89·95	1·116	1·302	2·466	2·103	1·335
1·490	47·4	98	76·80	89·60	169·69	144·70	91·90	1·144	1·335	2·528	2·156	1·369
1·495	47·8	99	78·52	91·60	173·48	147·93	93·95	1·174	1·369	2·593	2·211	1·404
1·500	48·1	100	80·65	94·09	178·19	151·96	96·50	1·210	1·411	2·672	2·278	1·447
1·501	...	...	81·09	94·60	179·16	152·78	97·03	1·217	1·420	2·689	2·293	1·456
1·502	...	...	81·50	95·08	180·07	153·55	97·52	1·224	1·428	2·704	2·306	1·465
1·503	...	...	81·91	95·55	180·96	154·31	98·00	1·231	1·436	2·720	2·319	1·473
1·504	...	...	82·29	96·00	181·81	155·04	98·46	1·238	1·444	2·735	2·332	1·481
1·505	48·4	101	82·63	96·39	182·55	155·67	98·86	1·244	1·451	2·748	2·343	1·488
1·506	...	...	82·94	96·76	183·25	156·27	99·27	1·249	1·457	2·759	2·353	1·494
1·507	...	...	83·26	97·13	183·95	156·86	99·62	1·255	1·464	2·773	2·364	1·502
1·508	48·5	...	83·58	97·50	184·65	157·47	100·00	1·260	1·470	2·784	2·374	1·508
1·509	...	...	83·87	97·84	185·30	158·01	100·35	1·265	1·476	2·795	2·384	1·514
1·510	48·7	102	84·09	98·10	185·79	158·43	100·62	1·270	1·481	2·805	2·392	1·519
1·511	...	...	84·28	98·32	186·21	158·79	100·84	1·274	1·486	2·814	2·400	1·524
1·512	...	...	84·46	98·53	186·61	159·13	101·06	1·277	1·490	2·822	2·406	1·528
1·513	...	...	84·63	98·73	186·98	159·45	101·26	1·280	1·494	2·829	2·413	1·532
1·514	...	...	84·78	98·90	187·30	159·72	101·44	1·283	1·497	2·835	2·418	1·535
1·515	49·0	103	84·92	99·07	187·63	160·00	101·61	1·287	1·501	2·843	2·424	1·539
1·516	...	...	85·04	99·21	187·89	160·22	101·75	1·289	1·504	2·848	2·429	1·543
1·517	...	...	85·15	99·34	188·14	160·43	101·89	1·292	1·507	2·854	2·434	1·546
1·518	...	...	85·26	99·46	188·37	160·63	102·01	1·294	1·510	2·860	2·439	1·549
1·519	...	...	85·35	99·57	188·58	160·81	102·12	1·296	1·512	2·864	2·442	1·551
1·520	49·4	104	85·44	99·67	188·77	160·97	102·23	1·299	1·515	2·869	2·447	1·554

Table for the Correction of the observed Specific Gravity of Nitric Acid for differences of Temperature between 13° and 17° C.

Specific Gravity.	Correction for ± 1°.	Specific Gravity.	Correction for ± 1°.
1·000—1·020	±0·0001	1·281—1·310	±0·0010
1·021—1·040	0·0002	1·311—1·350	0·0011
1·041—1·070	0·0003	1·351—1·365	0·0012
1·071—1·100	0·0004	1·366—1·400	0·0013
1·101—1·130	0·0005	1·401—1·435	0·0014
1·131—1·161	0·0006	1·436—1·490	0·0015
1·162—1·200	0·0007	1·491—1·500	0·0016
1·201—1·245	0·0008	1·501—1·520	0·0017
1·246—1·280	0·0009		

This table has been worked out for pure acids, and the values do not apply absolutely to observations made on commercial acids, which are never pure. Such differences may be considerable in the case of commercial nitric acid, owing to the presence of lower oxides of nitrogen, generally calculated to nitrogen peroxide. The influence of nitrogen peroxide on the specific gravity has been observed by many investigators,[1] but no method has been devised to allow for its effect when present. Lunge and Marchlewski[2] have shown that Hirsch's view, that 1 per cent. of nitrous acid corresponds to an increase of 0·01 in the specific gravity, is untenable. Their observations gave the following results for the strongest commercially important acid.

Specific Gravity of Initial Acid 1.4960 *at* 15°/4° (in vacuo).

N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.	N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.	N_2O_4 per cent.	Alteration of the Specific Gravity by N_2O_4.
0·25	0·00050	4·50	0·02875	8·75	0·05825
0·50	0·00075	4·75	0·03050	9·00	0·06000
0·75	0·00150	5·00	0·03225	9·25	0·06160
1·00	0·00300	5·25	0·03365	9·50	0·06325
1·25	0·00475	5·50	0·03600	9·75	0·06500
1·50	0·00675	5·75	0·03775	10·00	0 06600
1·75	0·00775	6·00	0·03950	10·25	0·06815
2·00	0·01050	6·25	0·04175	10·50	0·06975
2·25	0·01250	6·50	0·04300	10·75	0·07135
2·50	0·01425	6·75	0·04475	11·00	0·07300
2·75	0·01625	7·00	0·04650	11·25	0·07450
3·00	0·01800	7·25	0·04720	11·50	0·07600
3·25	0·01985	7·50	0·05000	11·75	0·07750
3·50	0·02165	7·75	0·05165	12·00	0·07850
3·75	0·02350	8·00	0·05325	12·25	0·08050
4·00	0·02525	8·25	0·05500	12·50	0·08200
4·25	0·02690	8·50	0·05660	12·75	0·08350

[1] Loring Jackson and Wing, *Chem. Zeit. Rep.*, 1887, **11**, 293; and, R. Hirsch, *Chem. Zeit.*, 1888, **12**, 911.

[2] *Z. angew. Chem.*, 1892, **5**, 10.

The following example, dealing with nitric acid containing nitrous acid, will illustrate the use of these tables. A sample of nitric acid was found to contain 2·93 per cent. N_2O_4, and to have a sp. gr. of 1·4994 at 20°. From the table on p. 493, which may be used without hesitation for temperatures lying somewhat below 13° or above 17°, it will be seen that the specific gravity becomes, at 15°, $1 \cdot 4994 + (0 \cdot 0016 \times 5) = 1 \cdot 5074$. According to the table on p. 493, 0·0180 must be deducted from this weight, for the 2·93 per cent. (or in round figures 3 per cent.) N_2O_4. This gives, therefore, a sp. gr. for the pure acid $= 1 \cdot 5074 - 0 \cdot 0180 = 1 \cdot 4894$. For this value the round figure 1·490 is taken from the table on p. 492, giving 89·60 HNO_3 as the percentage of the sample. If instead of this value, which takes account of the N_2O_4 present, the value (1·5074) obtained by simply correcting for temperature had been taken, the percentage of nitric acid found would have been given as $\frac{97 \cdot 13 + 97 \cdot 50}{2} = 97 \cdot 31$ obtained as the mean of 1·507 with 97·13 per cent. HNO_3 and 1·508 with 97·50 per cent. HNO_3; that is, instead of the correct value 89·60 per cent., the erroneous value of 97·31 per cent.

In the application of these high strength nitric acids to nitration it is customary to regard the whole of the N_2O_4 as inactive, and the table (p. 493) is calculated from this standpoint. It might in many cases be more accurate to regard half of the nitrogen peroxide as active, according to the equation :—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

A much smaller deduction should then be made, and for this a special table might advantageously be drawn up.

Lunge and Marchlewski have endeavoured to prepare similar tables to make allowance for the nitrogen peroxide present in nitric acid solutions of two lower strengths (sp. gr. 1·4509 and 1·4018), which are included in the range of commercial acids. They were not able, however, to obtain concordant results, apparently owing to the partial or complete conversion of the nitrogen peroxide into nitrous and nitric acids; such tables are still less possible for weaker acids (*cf.* p. 495).

Estimation of Nitrogen peroxide.—This estimation for the correction to be applied to the specific gravity reading of high strength nitric acid solutions (*cf.* p. 493) is carried out as follows:—The acid is allowed to flow slowly and in small quantities at a time, from an accurately calibrated burette, into a measured volume of semi-normal potassium permanganate solution (15·803 g. $KMnO_4$ per litre), warmed to 40°, until the colour disappears. The acid should be allowed to stand for some time in the burette before the titration is made, until

it has attained the temperature of the room as measured by an accurate thermometer; this is indicated by the volume remaining constant. The burette should be graduated in $\frac{1}{20}$ c.c., and it should be possible to read with certainty to 0·01 c.c. The number of c.c. of acid required to decolorise the permanganate solution, multiplied by the sp. gr. corresponding to the room temperature, gives the weight of acid used, from which the percentage content in N_2O_4 is calculated in the manner described under the examination of nitrous vitriol (p. 413). Each 1 c.c. $N/2$ permanganate solution corresponds to 0·02300 g. N_2O_4; thus with a consumption of n c.c. permanganate, and m c.c. of the acid under examination, the content in $N_2O_4 = \frac{0{\cdot}023n}{m}$ g. per c.c. The estimation of the three nitrogen acids in admixture is described in the section on Sulphuric Acid (p. 410).

The Total Acidity is generally determined in practice by the hydrometer only, notwithstanding the great uncertainty inseparable from the method in this particular case (*cf.* p. 493). It may, of course, be determined by titration, and this should be done in all important samples. This estimation can be carried out without difficulty in the case of slightly fuming acids, either by pipetting a quantity of the previously diluted acid or, preferably, by weighing out a portion of the concentrated acid in the bulb-tap pipette used for fuming sulphuric acid (Fig. 201, p. 463). In titrating, attention must be paid to the destructive action of nitrous acid on methyl orange. In the case of strongly fuming red acids, even the method of weighing in the special pipette fails to give satisfactory results, owing to the impossibility of completely washing out the nitrogen oxides, especially nitric oxide, which are continually evolved from the strong acid. On this account the following directions given by Lunge and Marchlewski should be adopted:—10 c.c. of the acid is allowed to drop slowly, preferably from a burette, into ice-cold water, the solution made up to 100 c.c., and an aliquot part titrated with a very accurately prepared standard sodium hydroxide solution.

The percentage of total nitrogen acids may also be determined in the nitrometer, employing the bulb form (Fig. 26, p. 81), so as to accommodate the large volume of nitric oxide evolved. The test is carried out exactly as described under the analysis of saltpetre, the quantities taken being 1 c.c. of the acid, measured in an accurate pipette, and 10 c.c. of concentrated sulphuric acid. This method is, however, only employed in samples in which a large proportion of sulphuric acid is already present, as, for example, in nitrating and spent acids.

Other Tests.—*Fixed residue.* This consists chiefly of sodium sulphate with small quantities of oxide of iron, etc., and is estimated by

evaporating 50 c.c. of the acid to dryness in a place protected from dust, igniting, and weighing.

Krauch[1] states that 10 g. of pure nitric acid should leave, on evaporation in a porcelain dish, only a very minute and scarcely weighable residue; on an average he obtained a residue of from 2 to 3 mg. from 50 g. of pure concentrated acid.

Sulphuric acid (Krauch): 10 g. is evaporated to about 1 c.c. in a porcelain dish, the residue dissolved in 30 c.c. of water, the solution transferred to a beaker, heated, and barium chloride added. No sign of a precipitate should appear in the case of acid. nitric. pur., even after standing for some time.

In carrying out this test, it is necessary to bear in mind that the presence of strong nitric acid retards the precipitation; the greater part of the nitric acid must either be removed by evaporation or nearly neutralised by the addition of chemically pure sodium carbonate.

For the quantitative determination of sulphuric acid the solution is rendered nearly neutral by the addition of pure sodium carbonate, and precipitated by barium chloride as described on p. 368. If the acid leaves an appreciable residue on evaporation, this must be taken into account, as it consists mainly of sodium sulphate.

Chlorine. (Krauch): 50 c.c. of distilled water to which a few drops of silver nitrate solution have been added should show no change on the addition of 5 to 10 c.c. of "pure" nitric acid. This method of carrying out the test removes any uncertainty which may arise should the distilled water employed not be absolutely free from chlorine.

For the quantitative estimation, the acid is neutralised with chemically pure sodium carbonate and titrated with silver nitrate solution; a very slightly alkaline reaction is not prejudicial.

Heavy metals and alkaline earths (Krauch): 20 g. is diluted with water and treated with excess of ammonia, ammonium sulphide, and ammonium oxalate. In the case of acid. nitric. pur., no darkening or cloudiness should be formed.

Iron is detected qualitatively by adding potassium thiocyanate to the previously diluted solution; quantitatively, by supersaturating the acid with ammonia, heating for some time, and collecting the precipitated hydroxide on an ash-free filter. Traces of iron are best determined colorimetrically by means of potassium thiocyanate according to the directions given by Lunge[2] (*cf.* p. 179 *et seq.*).

Iodine. Krauch states that nitric acid is coloured yellow by the presence of $\frac{1}{200}$ per cent. of iodine, and that it may be identified by

[1] *The Testing of Chemical Reagents for Purity*, trans. by H. B. Stocks, 1919, p. 201.

[2] *Z. angew. Chem.*, 1896, 9, 3.

shaking the acid with chloroform (Biltz). A yellow coloration may also be due to chlorine compounds, but is generally to be ascribed to the presence of lower nitrogen oxides. The iodine is not usually present in the free state, but as iodic acid dissolved in the nitric acid. The oxygen compounds of iodine, as well as iodine itself, are recognised by cautiously adding a very dilute solution of sulphurous acid or a few drops of sulphuretted hydrogen water to the diluted acid and extracting any iodine so liberated by carbon bisulphide, or testing by the addition of starch solution. An excess of sulphurous acid or of sulphuretted hydrogen vitiates the reaction.

An alternative method is to treat the solution with chemically pure zinc, which reduces the iodic acid, whilst the nitrous acid formed at the same time liberates iodine from the hydriodic acid produced. The solution is then well shaken with carbon bisulphide.

According to the Pharmaceutical Commission of the German Apotheker-Verein,[1] iodine and iodic acid are tested for by shaking the acid, diluted with twice its volume of water, with a small quantity of chloroform; the solvent should not be tinged violet even after the addition of a small piece of zinc to the acid solution.

Beckurts[2] gives the following as the most delicate test for iodine in nitric acid:—1 c.c. of the acid is boiled to remove lower oxides of nitrogen, and to oxidise all the iodine to iodic acid, and 1 c.c. of well-boiled water is then added, followed by a few drops of a solution of potassium iodide and starch in air-free water. A blue coloration indicates the presence of iodine in the original solution; a blank test made with the potassium iodide and pure acid is essential.

EXAMINATION OF NITRATING AND SPENT ACIDS. (MIXTURES OF SULPHURIC ACID, NITRIC ACID, ETC.)

Mixtures of sulphuric and nitric acids are prepared for coal-tar colour works and for explosives factories for nitrating purposes. On the other hand, waste acids are produced in these works, containing in addition to the original components (of which the greater portion of the nitric acid has naturally been utilised) much nitrous acid and a small quantity of organic matter. Residual acids which contain large amounts of organic matter, and have attained thereby a tarry consistency, as for example the acids from the purification of benzol and petroleum, will not be considered. They contain no nitric acid, and may be very considerably purified from the tarry matter by dilution; the tarry constituents consist, in the main, of pyridine bases, condensed hydrocarbons, etc.

[1] *Arch. Pharm.*, 1887, 93.

[2] *Fischer's Jahresber.*, 1886, 305.

According to Guttmann, the average composition of spent acid is as follows:—

	From Nitroglycerine.	From Nitrocellulose.	From Nitrobenzene, Picric Acid, etc.
HNO_3 . .	10	10	1
H_2SO_4 . .	70	80	65
H_2O . .	20	10	34
	100	100	100

No notice is taken in these data of lower nitrogen oxides or of organic matter.

The following constituents are estimated in nitrating and similar mixtures:—

1. **Total Acidity.**—Two to 3 g. is weighed off in the bulb pipette, allowed to flow cautiously into a large volume of water, and the total acid estimated by titration with normal sodium hydroxide solution. Litmus may be used as indicator, but if so, prolonged boiling is necessary; methyl orange may also be employed, notwithstanding the nitrous acid present, if the titration be carried out in the cold and the operation conducted as described on p. 449.

2. **Lower Nitrogen acids** are estimated by allowing the acid to flow into a measured volume of potassium permanganate solution; the method is more fully described under the testing of nitrous vitriol (p. 413; *cf.* also p. 494). They may be calculated to HNO_2 or N_2O_3 or to N_2O_4. The lower nitrogen oxides contained in the strong nitric acid consist mainly of N_2O_4; on mixing with concentrated sulphuric acid this is converted into equimolecular proportions of HNO_3 and of $SO_2(OH)(ONO)$. Each c.c. of seminormal permanganate solution used corresponds to 0·02300 g. N_2O_4; if therefore x represents the number of c.c. of permanganate taken, y the c.c. of acid required to decolorise this, and s the specific gravity of this acid, then the N_2O_4 content in g. per litre is equal to $\frac{23{\cdot}00x}{y}$, or in percentage by weight to $\frac{2{\cdot}300x}{ys}$.

3. **Total Nitrogen acids** are estimated in the nitrometer (p. 78). The value found, less that obtained in determination (2), gives the content of nitric acid, and the total acidity, less the total nitrogen acids, that of sulphuric acid.

Finch[1] has devised two methods for determining total nitrogen acids. In the first, 8 g. is diluted to a litre, and 50 c.c. of the solution is treated

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1912, 7, 13 and 337; *J. Soc. Chem. Ind.*, 1912, 31, 58 and 1028.

with excess of barium carbonate. The excess, with the precipitated barium sulphate, is filtered off and washed. To the filtrate a known quantity, in excess, of sodium carbonate solution is added, the precipitated barium carbonate filtered off and washed, and the excess of sodium carbonate in the filtrate determined by titration with acid. The amount used is equivalent to the nitric and nitrous acids. In the second method the total acidity is determined by titration with $N/10$ barium hydroxide and phenolphthalein. The liquid is boiled, some filter-pulp added, and the barium sulphate filtered off and washed. The filtrate is heated to boiling, and $N/5$ normal potassium chromate slowly added, till a drop colours the clear liquid yellow, showing that the barium nitrate and nitrite have been exactly decomposed.

Wuyts[1] uses a modified Schloesing method, in which a weighed quantity of the acid, diluted with water, is slowly run into a boiling acidified ferrous chloride solution, and the evolved nitric oxide collected and measured over water saturated with the gas. The volume is compared with that (approximately equal) evolved from a known weight of pure potassium nitrate, and hence the nitric acid equivalent of the total nitrogen acids deduced. The method is accurate, and very rapid when a number of successive determinations have to be made. For details of manipulation the original paper should be consulted.

Planchon[2] has devised a "Manonitrometer" for this and similar purposes, which diminishes error by allowing the use of larger quantities of substance. A strong flask has a stopper which can be clamped quite tight with the aid of a rubber washer and is provided with two exit-tubes, one with a stop-cock, communicating with a water-pump, the other joined to a barometer-tube dipping into mercury and having a scale and vernier. The flask is charged with 15 c.c. of mercury and 50 c.c. of concentrated sulphuric acid, and a vessel containing a weighed quantity (about 2·5 g.) of the substance to be analysed. It is closed, exhausted, and the scale adjusted to the height of the mercury. The materials are now shaken up till reaction is complete, the flask is immersed in water of known temperature, and the increase of pressure read when the mercury is steady. From the volume of the flask, temperature, and pressure, the amount of nitric oxide is calculated.

4. **Sulphuric acid.** Two to 3 g. is weighed in the bulb-pipette (Fig. 201, p. 463), transferred to a small porcelain dish, and heated on the water-bath for a half to one hour, a small quantity of water being at the same time added to destroy all nitrosyl-sulphuric acid. The heating is continued until on shaking the beaker all nitrous smell has disappeared. The removal of the nitric acid is facilitated by occasionally blowing on to the acid and rotating the dish. The contents are then

[1] *J. Soc. Chem. Ind.*, 1916, **35**, 149.
[2] *Ann. Chim. Anal.*, 1915, **20**, 189; *J. Soc. Chem. Ind.*, 1915, **34**, 1031.

washed into a beaker and titrated with normal or $N/2$ sodium hydroxide and methyl orange; this gives the sulphuric acid only.

Lunge and Berl[1] have shown that this method gives low results, and they recommend the determination of the sulphuric acid by difference from the total acidity less the total nitrogen acids, as given above.

The sulphuric acid may also be determined by precipitation as barium sulphate, but the above method effects a considerable saving of time, as a large number of samples can be evaporated simultaneously, and then only require to be titrated to complete the analysis.

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[1] *Z. angew. Chem.*, 1905, 18, 1687.

THE MANUFACTURE OF SALTCAKE AND OF HYDROCHLORIC ACID

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A. BRINE AND SALTWORKS

BRINE is regularly tested by the hydrometer both at the spot where it is obtained (bore-holes, etc.), and in the works where it is employed (saltworks, ammonia-soda works, etc.). The temperature at which the readings are made should of course be taken into account, and the accuracy of the hydrometer ascertained. The method of checking hydrometers, together with a description of the errors usually found in these instruments, will be found on p. 118 *et seq.*

A saturated solution of sodium chloride boils at 109·4°, and contains at this temperature between 29·4 and 29·5 per cent. of the salt.

The relationship between the specific gravity of salt solutions at 15° C. and the percentage content of salt is given in the following table by Gerlach :—

Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage NaCl.
1·00725	1	1·07335	10	1·14315	19
1·01450	2	1·08097	11	1·15107	20
1·02174	3	1·08859	12	1·15931	21
1·02899	4	1·09622	13	1·16755	22
1·03624	5	1·10384	14	1·17580	23
1·04366	6	1·11146	15	1·18404	24
1·05108	7	1·11938	16	1·19228	25
1·05851	8	1·12730	17	1·20098	26
1·06593	9	1·13523	18	1·20433	26·395

H. C. Hahn[1] has more recently determined the specific gravity of solutions of sodium chloride, reducing the values to water at 4°, and observing all possible precautions. Owing to the very special refinements used in the determinations, they are hardly applicable to technical conditions of work.

[1] *J. Amer. Chem. Soc.*, 1898, **20**, 621 ; *Chem. Centr.*, 1898, **II.**, 699.

Analysis of Brines and Mother Liquors

The following determinations are made :—

1. *Specific gravity*, by means of a densimeter or a hydrometer; in the latter case the hydrometer readings are reduced to sp. gr. by means of the table given on p. 124.

2. *Total Chlorine (expressed as sodium chloride).* Ten c.c. of the brine is diluted to 1000 c.c.; of this 10 c.c. is titrated with silver nitrate solution (*cf.* p. 507).

3. *Sulphuric acid.* Fifty c.c. of the brine is rendered acid by the addition of a few drops of hydrochloric acid, diluted with an approximately equal volume of water and, when hot, treated gradually with a hot solution of barium chloride. The settled precipitate is repeatedly washed by decantation with hot water, acidulated with hydrochloric acid, and finally well washed on the filter (*cf.* p. 368).

4. *Oxides of Iron, Aluminium, Calcium, and Magnesium.* Two hundred and fifty c.c. of the brine is warmed with a little nitric acid, ammonia added in excess, and the whole heated for some time; the precipitate is filtered, dissolved in hydrochloric acid, reprecipitated, and ferric oxide and alumina determined in the usual manner. The calcium and magnesium are determined in the filtrate as described on p. 510. The results are calculated in exactly the same manner as in the analysis of salt (p. 508).

5. *Bicarbonates of ferrous Iron, Calcium, and Magnesium.* Five hundred c.c. of the brine is boiled fairly vigorously in a tall beaker or Erlenmeyer flask, fresh water added, and the boiling and evaporation repeated several times. Finally, hot water is added to the highly concentrated solution to dissolve any separated salt, the solution filtered, the insoluble residue washed with hot water, then dissolved in hydrochloric acid and precipitated with ammonia solution, free from carbonate. The precipitation is repeated if necessary. The precipitate of ferric hydroxide is filtered off, dissolved whilst still moist in dilute sulphuric acid (1 : 4), reduced with zinc, the undiluted reduced solution titrated with permanganate solution, and the volume of permanganate necessary to produce a faint rose coloration in the solution alone deducted from the reading obtained. Calcium and magnesium are determined in the filtrate as described on p. 510 *et seq.* The bicarbonates found are entered in the analysis as carbonates, and the quantity so found must be deducted from the total calcium, magnesium, and ferric oxide obtained under 4, before calculating the rest of the calcium and magnesium to sulphates or chlorides. Calcium bicarbonate is, as a rule, present to an appreciable extent in brine (from 0·2 to 0·5 g. and more per litre); on the other hand, magnesium bicarbonate appears in much smaller quantity, and its determination may usually be neglected.

6. *Water*. The percentage of water is arrived at by deducting the sum of the weights of the solid constituents present in a litre, from the weight of the litre of brine.

The results are calculated on the litre of brine or mother liquor.

Sweeney and Withrow[1] recommend the following procedure for the examination of brines:—

Deposit on aeration. The sample is allowed to stand, with occasional shaking, for two or three days to aerate any iron compounds present. The height of the liquid in the bottle is marked and the whole is filtered and the deposited matter is washed (the washings being kept separate), dried, and ignited to constant weight. The volume of the sample is measured by ascertaining the capacity of the original container.

The *specific gravity* of the filtered brine at 15° C. is determined by the Westphal balance. The sp. gr. of the fresh brine is different from that of the sample after several days.

Total solids are determined on 25 c.c. of the filtered sample; the residue is dried at 160° C. to expel all the water. This high temperature causes a slight volatilisation of acidic radicles, so that the result is not strictly accurate.

Silica. Twenty-five c.c. of the filtered brine is acidified with 5 c.c. of hydrochloric acid and evaporated to dryness, and the residue dried at 120° C. or above for an hour; 5 c.c. of hydrochloric acid and 20 c.c. of water are added, the solution is warmed, filtered, and the residue washed free from chlorides. The filtrate is evaporated, acidified as before, and a second precipitate of silica is obtained. The combined precipitates are ignited in a platinum crucible and weighed. The residue is treated with sulphuric and hydrofluoric acids, and the loss of weight is reported as silica. The residue is added to the iron and alumina precipitate.

Iron and alumina. The filtrate and washings from the silica are treated with a few drops of nitric acid and 5 c.c. of hydrochloric acid, boiled a few minutes, and then made alkaline with ammonia, boiled until all the ammonia is expelled, allowed to stand, filtered, washed, and ignited in the crucible from which the silica has been expelled. A separation of the iron and alumina is seldom required.

Calcium. The filtrate from the iron and alumina is diluted to 250 c.c. Of this 25 c.c. is diluted to 150 c.c., the calcium precipitated as oxalate and ignited to oxide; or determined by dissolving it in dilute sulphuric acid and titrating with potassium permanganate. The calcium should be reported as sulphate and chloride.

Magnesium. In the combined filtrates and washings from the calcium the magnesium is precipitated with sodium hydrogen phosphate, ignited to $Mg_2P_2O_7$, weighed and calculated to bromide and chloride.

[1] *J. Ind. Eng. Chem.*, 1917, 9, 671; *J. Soc. Chem. Ind.*, 1917, 36, 924.

Barium and strontium should be looked for in the absence of sulphates. They are partially precipitated with the calcium and magnesium. When the proportion of barium and strontium is low, they may be neglected. *Ammonia* is seldom present in commercially important proportions.

Sulphuric acid. Fifty c.c. of the filtrate from the iron and alumina precipitate is diluted to 100 c.c., and whilst boiling, 10 per cent. barium chloride solution is slowly added with constant stirring. The precipitate is filtered, washed, and ignited in a porcelain crucible. It is then dissolved in a few c.c. of warm concentrated sulphuric acid and poured into 250 c.c. water, allowed to stand and then filtered, washed, ignited, and weighed. (This method of purifying the barium sulphate is very effective.) The sulphuric acid is reported as calcium sulphate.

Potassium and sodium. The filtrate from barium sulphate is used for determining the potassium and sodium, which are reported as potassium and sodium chlorides.

Chlorine. If the brine is alkaline to phenolphthalein, it must be neutralised with sodium bisulphate solution. Ten c.c. of the filtered (and neutralised) sample is diluted to 1 litre, and 10 c.c. of this is then diluted to 200 c.c. and titrated with standard silver nitrate solution, using potassium chromate as indicator. A standard solution of sodium chloride containing the same amount of chlorine as the sample used, is diluted to 200 c.c. and titrated with silver nitrate so as to show the amount of silver nitrate required to affect the indicator. The error so found must be deducted from the silver nitrate used for the sample. The bromine value must also be deducted.

Bromine. One hundred c.c. of the sample is made alkaline with sodium carbonate and evaporated to dryness, the residue dissolved in water and filtered into a 250 c.c. flask, made distinctly acid with sulphuric acid and made up to the 250 mark. Twenty-five c.c. of the acid liquid is placed in a 50 c.c. Nessler glass and chlorine added until the maximum colour is developed. Ten c.c. of carbon tetrachloride is added and the mixture shaken and compared with the colours produced by various amounts of standard sodium bromide solution. Having obtained a rough idea of the amount of bromine present, 25 c.c. of the acidified sample is treated with chlorine and carbon tetrachloride as before, poured into a wet filter and the water drained off. The filter is then punctured and the carbon tetrachloride is received in a 25 c.c. Nessler glass and compared with standard sodium bromide solution similarly treated. Traces of iodine present do not interfere and need not be reported. The bromine should be reported as magnesium bromide as it is so considered by the trade, but any free bromine should be reported as such.

B. SODIUM CHLORIDE (ROCK SALT)

Sodium chloride melts, according to Carnelly,[1] at 772° ; according to v. Meyer and Riddle,[2] at 815·4°. More recent determinations[3] give 801° as its solidifying point.

The commercial product may contain, in addition to moisture and water of hydration combined with calcium sulphate, etc., the following impurities: chlorides of calcium, magnesium, and potassium; sulphates of calcium, sodium, magnesium, and potassium; magnesium carbonate, organic substances (bitumen, mineral oil, gaseous hydrocarbons), and clay. According to the nature of the clay content, which seldom exceeds 0·1 per cent., the salt is coloured, usually a bluish green, but sometimes yellow, brown, reddish brown, or greenish (Schwarzenberg).

Other impurities which occur less frequently and only in traces, are: potassium bromide, potassium iodide, and lithium chloride, all of which, in consequence of their relatively greater solubility, accumulate in the mother liquors. Thus Krauch found in the concentrated mother liquors of brine from Werl, 3·3754 g. KBr, 0·0137 g. KI, and 8·9833 g. LiCl, per litre. Magnesium borate is found admixed with rock salt at Stassfurt. Occasionally the percentage of soluble foreign salts present is so great that the rock salt is rendered useless for food purposes.

An appreciable percentage of magnesium chloride (0·2 per cent. is sufficient) gives a sharp saline flavour to the salt and renders it hygroscopic, as do small quantities of calcium chloride.

1. Ordinary Salt

Sampling. For the method of taking an average sample, *cf.* p. 8.

Qualitative analysis. The salt is, from time to time, examined qualitatively for potassium, alkali bromides and iodides, and, when it is intended for culinary purposes, for metallic salts also (lead, copper, tin) which may have been taken up from the vessels used in the purification process. These metals are detected in the usual manner. A simple method of examining for the other impurities mentioned consists in extracting a considerable quantity of the salt with water, using an insufficient quantity to effect complete solution, evaporating the filtered extract to one-third of its bulk, again filtering, and dividing the filtrate into two portions. To the first portion platinic chloride is added and the mixture thoroughly shaken; a lemon yellow precipitate indicates the presence of potassium chloride. The second portion is treated with chlorine water, drop by drop, and shaken with chloroform after each

[1] *J. Chem. Soc.*, 1879, **35**, 280. [2] *Ber.*, 1893, **26**, 2447.
[3] *U.S. Bureau of Standards*, Circular No. 35, 3rd ed.; *Chem. News*, 1919, **118**, 130.

addition; any iodine present is liberated first, the bromine subsequently, and each may be recognised in turn by the colour imparted to the chloroform. (*Cf.* also p. 509 for Krauch's method of testing for iodine.)

Quantitative analysis. For works' purposes a shortened method of analysis is usually adopted. The constituents usually determined are moisture, total chlorine expressed as sodium chloride, sulphuric acid, calculated to calcium sulphate, and matter insoluble in water. These figures are amplified periodically by the determination of calcium, magnesium, ferric oxide, of the percentage insoluble in hydrochloric acid, sand, clay, etc., and also, by difference, the approximate amounts of calcium and magnesium carbonates present (cf. *infra*). The quantities of magnesium chloride, sodium sulphate, or calcium chloride, present may be arrived at by the following simple methods, which will be found sufficiently accurate for technical purposes.

1. **Water.**—(*a*) *Moisture.* Five g. of the salt is heated in a platinum crucible, well covered to prevent loss by decrepitation, at first very gradually and finally for some minutes at a low red heat. The loss in weight gives the total water present, that is, the moisture proper plus that chemically combined; the amount of the latter is usually very small. This method has the disadvantage that, no matter what care be taken, a small loss of salt always occurs owing to decrepitation. By employing as new a platinum crucible as possible, with smooth walls and a well-fitting lid, and placing the stand, Bunsen burner, etc., on a sheet of black glazed paper, the loss, which may reach 1 per cent. or over, is very much diminished; but the method lacks certainty and cannot be carried out quickly or without direct attention. In works where dozens of water determinations, including those of damp salt, which may contain up to 15 per cent. of water, have to be made, the inaccuracy of the method is very pronounced.

Böckmann consequently recommends the following method, which, whilst perfectly accurate, permits of a large number of water determinations being made simultaneously and without special attention during the drying process.

A dry Erlenmeyer flask, about 14 to 15 cm. high, and of about 250 c.c. capacity, is weighed together with a dry funnel inserted in the neck. About 5 g. of salt are then introduced into the flask, this quantity being just sufficient to form a thin layer on the bottom, and the flask, funnel, and salt accurately weighed. The object of the funnel is to allow the dried salt to be cooled in the open instead of in a desiccator, and to prevent loss of salt by decrepitation during the expulsion of the combined water described under (*b*). The flask is then placed on a previously warmed, portable sand-bath, 40 cm. by 20 cm., large enough to carry eight flasks, the temperature of the sand being about 140° to 150°. The funnels are removed, and placed

each near its corresponding flask, on the bench. The water soon begins to come off, condensing at the start on the upper portions of the flasks; at the end of three to four hours all the water present as moisture is driven off from the salt without any crackling sound. The funnels are replaced in the flasks, which are then allowed to cool on a thick glass or marble slab, and weighed.

(*b*) *Chemically combined Water.* After the determination of the moisture the flasks are carefully heated on wire gauze, or on a silica or metal (aluminium) plate, over the free flame, with the funnels in position, to prevent loss by decrepitation. The water held in chemical combination by calcium sulphate, etc., is thus driven off; the evolution of this small quantity of water is accompanied by violent crackling. Since the amount of combined water present is very frequently under 0·1 per cent. and seldom more than $\frac{1}{4}$ to $\frac{1}{3}$ per cent., its determination can usually be omitted in technical analyses.

2. **Total Chlorine (expressed as Sodium chloride).**—Ten g. of the finely ground average sample is dissolved in lukewarm water, and after cooling, made up to 500 c.c. at 15° in a measuring flask. Ten c.c. of this solution, corresponding to 0·2 g. salt, is diluted with 100 c.c. of water, 10 drops of a 10 per cent. potassium chromate solution added, and the whole titrated with silver nitrate solution (p. 73). A deduction of 0·2 c.c. silver nitrate solution is made from the observed reading, since this quantity is necessary to produce the red colour with the chromate. Each c.c. of $N/10$ silver nitrate solution equals 0·005850 g. NaCl.

3. **Sulphuric acid.**—Ten g. of the sample is dissolved in lukewarm water and a little hydrochloric acid added; should much earthy matter be present the salt should be digested for some time with hydrochloric acid, to ensure complete solution of the calcium sulphate present. The cooled solution is then made up to 500 c.c. and passed through a dry, pleated filter. Two hundred and fifty c.c. of the filtrate is heated to boiling and precipitated by the addition of hot barium chloride solution in slight excess. The barium sulphate is first washed by decantation with water acidulated with hydrochloric acid, and finally on the filter (*cf.* p. 368).

4. **Matter insoluble in water and acids, Calcium and Magnesium.**—Fifty g. of the finely ground average sample is dissolved in warm water and filtered through a filter paper previously tared against one of equal weight. The insoluble matter is carefully washed from the filter into a small glass mortar and ground with sufficient water to dissolve all the gypsum present. The water is decanted through the filter and the operation repeated a few times. The insoluble matter is again collected on the filter and dried at 100°; the weight obtained represents the matter insoluble in water (clay, sand,

oxide of iron, calcium carbonate, etc.). This residue is then treated on the filter with warm dilute hydrochloric acid, the solution obtained precipitated by the addition of ammonia, the precipitated ferric hydroxide dissolved in dilute sulphuric acid (1 : 4), and the iron determined, after reduction by zinc, by titration with permanganate solution. The residue insoluble in hydrochloric acid is well washed with water, dried at 100°, and weighed to give the percentage of sand and clay. The difference between the sum of the weights of the sand, clay, and iron oxide, and the weight of the total matter insoluble in water, may usually be regarded as representing the carbonates of calcium and magnesium present.

The calcium and magnesium are determined in the filtrate from the matter insoluble in water and in hydrochloric acid in the usual manner after addition of ammonium chloride and ammonia (*cf.* p. 510).

Calculation of Results. All magnesium found is calculated to magnesium chloride and its equivalent in sodium chloride deducted from the "total" sodium chloride, to give the actual content of the latter. Should more sulphuric acid be found than corresponds to the soluble calcium, such excess is calculated to sodium sulphate. In the reverse case the excess of calcium is calculated to calcium chloride, and a corresponding deduction made in arriving at the percentage of sodium chloride.

J. and S. Wiernik[1] recommend a direct determination of the magnesium chloride present in sodium chloride and in brine, and they further state that wholly incorrect results may be obtained by the usual method of calculation. They extract the dried salt with absolute alcohol, which dissolves out magnesium chloride only, and, after evaporating off the alcohol, determine either the magnesium as pyrophosphate or the chlorine by titration. Both methods should give the same result when expressed as magnesium chloride. The total calcium, magnesium, chlorine, and sulphuric acid are determined in the original solution in the usual manner. The sulphuric acid found is first calculated on the calcium, then on the excess of magnesium that may be present above that found as magnesium chloride by extraction with alcohol; any sulphuric acid still remaining is regarded as sodium sulphate. Chlorine found as magnesium chloride is deducted from the figure obtained for "total chlorine," and the difference stated in terms of sodium chloride.

All such calculations are quite illusory in the case of dilute solutions where the salts are either almost completely ionised or in part dissociated hydrolytically; in solid salts and concentrated solutions such as the above, however, the greater part of the salts are actually present as such.

[1] *Z. angew. Chem.*, 1893, 6, 43.

2. Pure Sodium Chloride for Analytical Purposes

Pure sodium chloride appears under various names, and these preparations often contain traces of sulphates of calcium or magnesium.

Krauch's method of examining "pure" sodium chloride is as follows:—

Complete Solubility and freedom from Sulphate.—Three g. of salt and 20 c.c. of water should yield a clear, neutral solution, which, when diluted to 80 c.c., heated to boiling, and treated with barium chloride, should show no sign of a precipitate even after standing for several hours.

Examination for Alkaline Earths and heavy Metals.—Three g. of the salt is dissolved in 50 c.c. of water, the solution heated to boiling, and ammonium oxalate, sodium carbonate, and ammonium sulphide added. No turbidity should result.

Iodine.—Twenty c.c. of the aqueous solution (1 : 20) treated with one drop of ferric chloride solution and a little starch solution should show no blue coloration.

Potassium.—The concentrated solution of the salt should give no precipitate on addition of platinic chloride even after long standing.

C. SULPHURIC ACID

The examination of sulphuric is conducted as previously described (p. 429 *et seq.*). The acid employed in the manufacture of saltcake is either non-purified chamber acid, Glover acid, or acid concentrated in pans placed over the pyrites burners. The acid employed in the preparation of saltcake intended for use in the manufacture of the better qualities of glass should be as far as possible free from iron. The determination of the iron is described above (p. 452 *et seq.*).

D. SALTCAKE

The saltcake drawn from the furnaces is spread out in long ridges on a stone-paved floor to cool. Samples are taken morning and evening, corresponding to the output of each furnace, from various places in the several rows, and an average of the lots so taken ground in a suitable mill.

For works' purposes, determinations 1 and 2 given below are

sufficient; for purposes of sale or purchase, the other tests given should be made.

1. **Free Acid.**—Twenty g. of the saltcake is dissolved in water and made up to 250 c.c.; 50 c.c. of this solution is titrated with normal sodium hydroxide solution, using litmus or methyl orange as indicator. Each 1 c.c. alkali corresponds to 1 per cent. SO_3. All acidity, whether arising from HCl, $NaHSO_4$, or from iron and aluminium salts of acid reaction, is calculated to SO_3. Should large quantities of iron and aluminium salts be present, and it be desired to avoid the influence of these in this determination, no indicator is added to the solution, but the end-reaction is judged by the first appearance of a permanent flocculent precipitate, which occurs as soon as the free acid and the acid sulphate have been neutralised by the alkali.

2. **Sodium chloride.**—Fifty c.c. of the solution prepared under 1 is exactly neutralised by the addition of the necessary volume of normal sodium hydroxide solution, and the neutral solution titrated with $N/10$ silver nitrate solution after the addition of a little potassium chromate solution (*cf.* p. 73). Each 1 c.c. silver nitrate solution, after deducting 0·2 c.c. from the total as allowance for the end-reaction, corresponds to 0·146 per cent. NaCl. With high-grade saltcake a solution containing 2·9054 g. $AgNO_3$ per litre should be employed, each 1 c.c. of which corresponds to 0·001 g. NaCl, or, with the above amount of saltcake, to 0·025 per cent. NaCl.

3. **Iron.**—Ten g. of the saltcake is dissolved in water, the iron reduced by addition of zinc and sulphuric acid and titrated with permanganate solution (p. 452). Very small amounts are estimated colorimetrically (p. 453). According to Ost,[1] sulphate manufactured in lead pans contains from 0·009 to 0·029 per cent., and that manufactured in iron pans 0·062 to 0·130 per cent. Fe.

4. **Insoluble Matter**, when present, is determined in the usual way.

5. **Calcium.**—Ten g. of the saltcake is dissolved in water, a little hydrochloric acid being added if necessary, and the solution treated with ammonium chloride and then ammonia in slight excess. The ammoniacal solution is heated to boiling and the calcium precipitated by the addition of a boiling solution of ammonium oxalate in considerable excess. The solution is allowed to stand for twelve hours, and the precipitate then washed with boiling water several times by decantation and finally on the filter, a small quantity of ammonium oxalate being added to the wash-water. The filter paper and precipitate are dried and burnt off in a platinum crucible (this may be done whilst the precipitate is still slightly moist), after which the whole is strongly ignited for twenty minutes over a Méker or Teclu burner. Should the precipitate be large in amount, which is unlikely, it must be

[1] *Z. angew. Chem.*, 1896, 9, 9.

heated in the blowpipe flame until the weight becomes constant. The precipitate is regarded as CaO; any ferric oxide present must, of course, be deducted. The desiccator used must prevent access of moisture and carbon dioxide.

Should any considerable quantity of magnesium be present—which is never likely to occur, however, in saltcake—the washed calcium oxalate precipitate must be transferred to a beaker, dissolved in a little warm hydrochloric acid, and reprecipitated by the addition of 2 to 3 c.c. of ammonium oxalate followed by ammonia in slight excess. The precipitate is allowed to settle for twelve hours and the reprecipitated calcium oxalate treated as above. The two filtrates are then combined for the magnesium determination.

Instead of converting the calcium oxalate to oxide and weighing, it may be dissolved in dilute sulphuric acid and titrated with permanganate solution, calculating the calcium from the oxalic acid thus found. Of course, in this case it is inadmissible to add ammonium oxalate to the water employed for washing; yet its omission may lead to a loss which is by no means negligible. Walland[1] overcomes this difficulty by standardising the permanganate solution against calcium oxalate prepared from pure calcium oxide obtained by ignition of the carbonate, and treated in exactly the same way as the precipitate obtained in the actual analysis, so that the errors are the same in the two cases.

Such a method always has disadvantages, and is only to be recommended when, as in technical work, a large number of analyses have to be made simultaneously; otherwise it offers no saving of time as compared with the ordinary method by ignition.

6. **Magnesium** is determined by addition of ammonium phosphate to the filtrate from operation 5. For very exact work this addition should be made in neutral solution and as far as possible in the absence of ammonium salts, the necessary ammonia being added subsequently. The filtrate from 5 should therefore be evaporated to dryness and, after gentle ignition to drive off the ammonium salts, extracted with a small quantity of hydrochloric acid. The solution is filtered from any separated carbonaceous matter, exactly neutralised with ammonia, heated to boiling, and sodium phosphate solution added, drop by drop, to the boiling solution until no further precipitation results. The mixture is allowed to cool, ammonia solution equal to one-third of its volume added, and the whole allowed to stand for three hours, or should only a small amount of magnesium be present, for twelve hours, before filtering. The precipitate is washed with 2½ per cent. ammonia solution, dried, separated as completely as possible from the filter paper, the latter burnt separately in a spiral of platinum wire, and the ash and

[1] *Chem. Zeit.*, 1903, **27**, 922.

precipitate then ignited, first at a low heat and finally strongly. The precipitate is thus converted to pyrophosphate, $Mg_2P_2O_7$, one part of which corresponds to 0·3621 part of MgO.

In the analysis of saltcake it is usual to precipitate the magnesium by direct addition of sodium phosphate to the filtrate from 5 without removing the ammonium oxalate, and observing the other precautions given; in this case the precipitate should be allowed to stand twenty-four hours before filtering.

This method of separating calcium and magnesium is essentially in accord with the conditions given by Treadwell.[1] An alternative method, differing somewhat from the above, has been described by T. W. Richards.[2] The magnesium salts must not be present in the solution in greater concentration than corresponds to $\frac{1}{50}$ normal. Ten equivalents of ammonium chloride are added to the solution, followed by oxalic acid in sufficient quantity to combine with the whole of the calcium. It is advantageous to reduce the dissociation of the oxalic acid by the previous addition of three or four equivalents of hydrochloric acid. A drop of methyl orange is added, the solution boiled, and very dilute ammonia added gradually at intervals during half an hour and with continued stirring. When the solution has been made neutral, a large excess of ammonium oxalate is added, and the whole allowed to stand for four hours. The precipitated calcium oxalate is thoroughly washed with water containing ammonium oxalate. The filtrate contains the whole of the magnesium with the exception of 0·1 to 0·2 per cent., which causes a corresponding error in the calcium, the whole of which is contained in the precipitate.

Heraeus[3] states that both platinum and platinum-iridium crucibles are easily injured by the ignition of magnesium ammonium phosphate. The effect takes place, however, in a very irregular manner, and is to be attributed to the liberation of phosphorus, which occurs at 900°, arising partly from the presence of carbon or reducing gases, and also partly from the hydrogen liberated by the decomposition of ammonia at the high temperature. The action due to ammonia is stronger if free ammonium phosphate be present in the precipitate, and may very easily occur if Gooch crucibles are used in which old precipitates have been allowed to remain. The action is most marked when the heating is carried out rapidly in a covered crucible. Up to the present it has not been possible to define the conditions under which the crucibles are least attacked.

Calcium and magnesium can be determined rapidly, and for many purposes sufficiently exactly, by adding sodium carbonate to the filtrate from the silica, ferric oxide, and alumina, evaporating to dryness,

[1] *Analytical Chemistry*, 5th edition, vol. ii., p. 76.

[2] *Z. anorg. Chem.*, 1901, **28**, 88.

[3] *Z. angew. Chem.*, 1902, **15**, 917.

igniting to remove the ammonium salts, taking up with sodium carbonate solution, extracting with hot water and weighing the calcium and magnesium carbonates remaining in the dish after drying at 200°; or by weighing as mixed oxides after ignition. The quantity of each base present may be determined indirectly from the difference in weight between the mixed carbonates and the mixed oxides; it is, however, better for this purpose to convert both into the sulphates. Christomanos[1] has applied this method to the analysis of a large number of samples of magnesite, but, like all indirect methods, it may lead to somewhat large errors.

7. **Aluminium.**—A considerable quantity of ammonium chloride or of ammonium nitrate is added to the solution of the saltcake, the mixture heated nearly to boiling in a porcelain or platinum dish and ammonia added, but not in too great excess, so as to avoid the removal of an excess by boiling off; the precipitate is then washed three times by decantation with hot water to which one drop of ammonia has been added, thoroughly washed on the filter with hot water, and dried on the pump. Any small quantities adhering to the sides of the dish are wiped off with a piece of filter paper. The filter paper and precipitate may be ignited, whilst still moist, in a platinum crucible, and finally ignited strongly, preferably over the blowpipe. The weight of ferric oxide, as found under 3, must be deducted from the weight obtained.

The ammonia employed must be tested by barium chloride for freedom from carbonate, which, if present, would cause precipitation of the calcium; if necessary, it should be purified by distillation over lime.

8. **Sodium sulphate.**—One g. of the sample is dissolved in water, the calcium, together with the iron, precipitated as under 5, the solution filtered, and the filtrate, after the addition of a few drops of pure sulphuric acid, evaporated to dryness. The dried residue is ignited, first alone, and again after the addition of a small piece of ammonium carbonate, and weighed. From the weight obtained there must be deducted (*a*) the sulphate equivalent of the sodium chloride found under 2 (1·000 g. $NaCl = 1{\cdot}215$ g. Na_2SO_4, or 1 c.c. $N/10$ silver nitrate solution $= 0{\cdot}00171$ g. Na_2SO_4), and (*b*) the magnesium sulphate equivalent of the magnesium found under 6 (1·000 g. $MgO = 2{\cdot}9856$ g. $MgSO_4$). The residue represents the Na_2SO_4 actually present in the original 1 g. of saltcake. If the magnesium sulphate alone be deducted from the gross weight of the sulphate found, the total sodium in the sample, expressed as sulphate, is obtained.

Isbert and Venator[2] proceed as follows:—About 2 g. of the saltcake is dissolved in the least possible volume of hot water; ferric oxide, alumina, calcium carbonate, and magnesium carbonate are precipitated

[1] *Z. anal. Chem.*, 1903, **42**, 606.

[2] *Z. angew. Chem.*, 1889, **2**, 66.

by the addition of ammonia and ammonium carbonate, the precipitate dissolved in hydrochloric acid and reprecipitated, the precipitate well washed with hot water, and the total filtrate collected in a platinum dish. The filtrate—which is about 100 c.c. in volume and contains, in addition to the sulphate, ammonium sulphate equivalent to the free acid, and sodium chloride—is treated with ammonium sulphate or sulphuric acid, and evaporated on the water-bath to convert the chloride into sulphate. The residue is gently ignited, to volatilise all ammonium salts, and weighed. From the weight of Na_2SO_4 so obtained, the weight of sulphate corresponding to the chloride present in the original sample must be deducted.

E. HYDROCHLORIC ACID

The daily control of the process in the works is confined to measuring the strength of the acid flowing from the condensers, jars, etc., and to determining the completeness attained in the absorption. The strength of the acid is measured by means of the hydrometer, and in some works tests are only taken once in the day. It is, however, preferable to allow the acid, as it leaves the plant, to flow through a glass cylinder in which the hydrometer floats; in this way the strength of the acid can be seen at any moment or a continuous record can be obtained if desired (p. 133).

It is especially important to check the amount of acid which escapes condensation and so passes into the atmosphere. Should the air be damp a practised eye can, to a certain extent, judge the degree of absorption by the appearance of the escaping vapours. Whilst white fumes are continually evolved from the open pipes of the pan condensers, even when condensation is complete, these consist entirely of steam, and may be distinguished from hydrochloric acid fume by the ease with which they are dissipated in the air. Hydrochloric acid vapour, on the other hand, forms dense white fumes, which, in a moist atmosphere, spread to form a heavy cloud over a considerable area, and persist for a considerable time. Very frequently the fumes only become apparent when the gases come into contact with the outer air.

According to the Alkali Act (1906), 95 per cent. of all the hydrochloric acid produced in a works must be condensed, and no gases are permitted to escape into the atmosphere which contain more than $\frac{1}{5}$ grain HCl per cubic foot (= 0·457 g. per cubic metre); and the total acidity of all the gases present must not exceed the equivalent of 4 grains SO_3 per cubic foot (= 9·15 g. per cubic metre). In these regulations the volume of the gases is reduced to 60° F. (15·5° C.) and 30 inches mercury (almost exactly 760 mm.).

Examination of the Exit Gases.—The examination of the chimney

gases is carried out in a Fletcher bellows, which serves both as aspirator and absorbing vessel. They are constructed to draw $\frac{1}{10}$ of a cubic foot of gas at one aspiration, but they should in all cases be standardised by filling with air at the normal working capacity and measuring the volume aspirated by expelling it into an inverted graduated vessel filled with water, correcting the volume obtained for temperature and pressure. In examining chimney or other gases the bellows are connected with the chimney by means of a porcelain, glass, or platinum tube, of 12 mm. diameter, which extends some considerable distance into the chimney. Both bellows and tube are first washed out with distilled water, 200 to 300 c.c. of distilled water then introduced, and the necessary number of aspirations made. The contents of the bellows are well shaken after each aspiration to allow all the acids present to be dissolved by the water. When the operation is complete, a little water is forced into the connecting tube and allowed to flow back into the bellows to wash out any acid that may have condensed in the tube. The liquid in the bellows is then washed into a porcelain dish, and if necessary filtered from soot. Any sulphurous acid present is oxidised by potassium permanganate, excess of the latter removed by a trace of ferrous sulphate, the solution neutralised by pure sodium carbonate, a little potassium chromate added, and the whole titrated with $N/10$ or $N/100$ silver nitrate solution. Each 1 c.c. $N/10$ silver nitrate solution $=0{\cdot}003646$ g. HCl.

In the Alkali Inspector's Report for 1898 (No. 35) an addition of hydrogen peroxide, free from chlorine, to the water put into the bellows was recommended. This addition effects the immediate oxidation of any sulphurous acid present in the gases. The total acidity is determined by titration with sodium carbonate solution, and subsequently the chloride as above, by means of silver nitrate. When working in this manner difficulties are liable to occur through discoloration which arises owing to incomplete oxidation of organic matter by the hydrogen peroxide, and this may under certain conditions lead to the reduction of the chromate; further, it is difficult to obtain hydrogen peroxide free from chlorine. For these reasons the process is now carried out as follows. The total acidity is determined as before with sodium carbonate solution and methyl orange, a few drops of potassium permanganate solution being added in cases where the solution is very dark owing to the presence of sooty matter. The neutralised solution is treated with 0·5 g. of calcium or magnesium carbonate, followed by 5 to 10 drops of a 5 per cent. ferric sulphate solution, the mixture stirred for a minute and then decanted or filtered. The chloride is then determined in the filtrate in the usual manner. The addition of ferric sulphate gets rid of the organic matter which is carried down with the ferric carbonate precipitate, and so gives a neutral solution in

which the hydrogen peroxide will not exert any reducing action on the chromate; also, it precipitates the arsenic and copper which are found in testing the gases from copper works.

The potassium permanganate, added to oxidise the organic matter, must be employed with caution, since the manganese sulphate produced may reduce the chromate, with the production of a green-coloured solution; this will not occur, however, if the solutions are neutralised as described.

If any of the above difficulties occur, it is best to oxidise with nitric acid and determine the chloride by Volhard's method (p. 74).

A continuous test may of course be made, as of the exit gases of the sulphuric acid process (p. 397), by employing a large aspirator and selecting a suitable type of absorption apparatus (*cf.* p. 398); the flasks described in the Alkali Inspector's Annual Report for 1897 are specially suitable for this purpose. A useful summary of these and other methods used by the Alkali Inspectors will be found in the *Technical Index to the Alkali Reports*, published (1919) by H.M. Stationery Office.

Examination of the Gases in the Hargreaves' Process

In this process[1] the burner gases from pyrites or blende are drawn, together with steam, through hot salt, packed in iron cylinders, whereby the sodium chloride is converted into sodium sulphate, the sulphur dioxide being gradually absorbed and hydrochloric acid liberated. The progress of the reaction is followed by withdrawing and testing samples of the gases passing through the connecting pipes between adjacent cylinders. The tests are made in the following manner:—

(*a*) *Total acidity*, best estimated by Lunge's method (p. 398).

(*b*) *Sulphur dioxide*, by Reich's method (p. 394).

(*c*) *Hydrochloric acid.* The test is made in the sample taken for test *a* by titration with silver nitrate, either by Mohr's method (p. 73), or by Volhard's method (p. 74).

The content of sulphur trioxide is obtained by deducting $b+c$ from a.

For continuous works tests, *a* or *b* may be omitted; either of these in combination with test *c* is sufficient.

Properties of Hydrochloric Acid

The strength of the acid is usually determined by the hydrometer. The use of the Twaddell scale (see p. 119) possesses the advantage that for acids of ordinary strengths the number of the degrees Tw. and the percentage of HCl in the acid are represented by practically the same

[1] *Cf.* Cumming, *Hydrochloric Acid and Saltcake*, 1923, p. 196 *et seq.*

figure. The following table, drawn up by Lunge and Marchlewski,[1] gives for the various specific gravities of pure hydrochloric acid the corresponding degrees on the Twaddell scale, the percentage content in HCl, the percentage content in acid of 28°·5 Tw. and of 30°·4 Tw., and the weight of HCl in grams per litre and in pounds per cubic foot.

Specific Gravity of Hydrochloric Acid Solutions at 15° C., compared with Water at 4°, and reduced to vacuum.

(Lunge and Marchlewski.)

Degrees Twaddell.	Specific Gravity at $\frac{15^{\circ}}{4^{\circ}}$ (*in vacuo*).	100 parts by weight correspond to parts by weight of			1 litre contains grms. HCl.	1 cubic foot contains lbs. HCl.
		HCl.	Acid of Sp. Gr. 1·1425 = 28°·5 Tw.	Acid of Sp. Gr. 1·152 = 30°·4 Tw.		
0	1·000	0·16	0·57	0·53	1·6	0·10
1	1·005	1·15	4·08	3·84	12	0·75
2	1·010	2·14	7·60	7·14	22	1·37
3	1·015	3·12	11·80	10·41	32	1·99
4	1·020	4·13	14·67	13·79	42	2·62
5	1·025	5·15	18·30	17·19	53	3·30
6	1·030	6·15	21·85	20·53	64	3·99
7	1·035	7·15	25·40	23·87	74	4·61
8	1·040	8·16	28·99	27·24	85	5·30
9	1·045	9·16	32·55	30·58	96	5·98
10	1·050	10·17	36·14	33·95	107	6·67
11	1·055	11·18	39·73	37·33	118	7·35
12	1·060	12·19	43·32	40·70	129	8·04
13	1·065	13·19	46·87	44·04	141	8·79
14	1·070	14·17	50·35	47·31	152	9·48
15	1·075	15·16	53·87	50·62	163	10·16
16	1·080	16·15	57·39	53·92	174	10·85
17	1·085	17·13	60·87	57·19	186	11·59
18	1·090	18·11	64·35	60·47	197	12·28
19	1·095	19·06	67·73	63·64	209	13·03
20	1·100	20·01	71·11	66·81	220	13·71
21	1·105	20·97	74·52	70·01	232	14·46
22	1·110	21·92	77·89	73·19	243	15·15
23	1·115	22·86	81·23	76·32	255	15·90
24	1·120	23·82	84·64	79·53	267	16·65
25	1·125	24·78	88·06	82·74	278	17·33
26	1·130	25·75	91·50	85·97	291	18·14
27	1·135	26·70	94·88	89·15	303	18·89
28	1·140	27·66	98·29	92·35	315	19·64
29	1·145	28·61	101·67	95·52	328	20·45
30	1·150	29·57	105·08	98·73	340	21·20
31	1·155	30·55	108·58	102·00	353	22·01
32	1·160	31·52	112·01	105·24	366	22·82
33	1·165	32·49	115·46	108·48	379	23·63
34	1·170	33·46	118·91	111·71	392	24·44
35	1·175	34·42	122·32	114·92	404	25·19
36	1·180	35·39	125·76	118·16	418	26·06
37	1·185	36·31	129·03	121·23	430	26·81
38	1·190	37·23	132·30	124·30	443	27·62
39	1·195	38·16	135·61	127·41	456	28·43
40	1·200	39·11	138·98	130·58	469	29·24

[1] *Z. angew. Chem.*, 1891, 4, 135.

The correct specific gravity at 15° C. may be calculated from readings made between 13° and 17° (and also for temperatures slightly below or above this range) by the aid of the accompanying short table. If the observed reading is made below 15° the values given in the table must be deducted for each 1° below the 15°; for observations made above 15° the corresponding values must be added.

Spec. Grav.	1·000—1·040:	± 0·0002
"	1·041—1·085:	0·0003
"	1·086—1·120:	0·0004
"	1·121—1·155:	0·0005
"	1·156—1·200:	0·0006

Kremers[1] has published a table giving the variations in the specific gravity of hydrochloric acid over a temperature range from 0° to 100° (normal temperature 19°·5); the most recent table is that of Fuchs.[2]

DETECTION OF IMPURITIES[3]

1. *Residue.** Ten g. should leave not more than a very minute and scarcely weighable residue on evaporation.

According to Krauch, the preparation of absolutely chemically pure hydrochloric acid is attended by considerable difficulties; he invariably found, on evaporating 50 g. of the acid in a porcelain dish, a residue of about 1 mg., probably consisting of calcium oxide derived from the porcelain vessel or from the sulphuric acid.

2. *Sulphuric acid.** (*a*) Five g. is diluted with 50 c.c. of water, and barium chloride added; no sign of a precipitate should appear after twelve hours' standing.

(*b*) Five hundred g. is slowly evaporated on the water-bath till only about 1 c.c. remains and the sulphuric acid determined in this residue, an ash-free filter paper being employed. The weight of barium sulphate found should not exceed 12 mg., corresponding to 1 mg. H_2SO_4 per 100 g. hydrochloric acid.

Krauch states that scarcely a single sample of the various makes to be found on the market is absolutely free from sulphuric acid when tested as under *b*; many of the samples examined gave the sulphuric acid reaction with test *a*, that is, without evaporating off the hydrochloric acid, showing, therefore, a greater degree of impurity than should be accepted.

In commercial work the evaporation of the acid may be omitted and much time saved by nearly neutralising the acid with pure sodium carbonate before precipitating by barium chloride.

[1] *Pogg. Ann.*, 1859, 108, 115. [2] *Z. angew. Chem.*, 1898, 11, 753.

[3] The tests marked with an asterisk are due to Krauch and apply only to acid. hydrochloric. purum. conc.

Lunge's method, which is rapid and suitable for works purposes, is based on the degree of turbidity produced by addition of barium chloride, and is best carried out in the following modified form proposed by Rürup.[1] Glass tubes having a lower part 6 mm. diameter, sealed below, and an upper part 15 mm. diameter, closed with a rubber stopper, are used for the estimation; the cylindrical, narrower portion is 250 mm. in length, and is graduated in the following manner. Acids containing varying proportions of sulphuric acid, from 0·4, 0·6, etc., to 3·0 per cent. SO_3, are prepared, 10 c.c. of each heated to boiling, transferred to the tube, nearly neutralised with strong ammonia, precipitated by addition of hot barium chloride solution and allowed to settle. A mark is then made on the tube corresponding to the level of the settled precipitate and the corresponding percentage of acid etched at the side. To carry out a test, 10 c.c. of the acid is nearly neutralised with ammonia, heated to boiling, transferred to the tube, 5 c.c. of a saturated solution of barium chloride added, the rubber stopper inserted, and the tube well shaken. Five minutes are allowed for settling before reading off the volume of the precipitate. The method is said to be accurate to within 0·05 per cent.

3. *Arsenic.* The detection and estimation of arsenic in hydrochloric acid is of importance not only in chemico-legal investigations but also in numerous analytical and technical applications. The methods of estimating arsenic in sulphuric acid apply also to hydrochloric acid (*cf.* p. 433 *et seq.*).

(*a*) According to Krauch, hydrochloric acid which will satisfy the following test may be looked upon as sufficiently pure for most analytical work. Ten g. of the acid is diluted with 10 c.c. of water and the mixture carefully covered in a test tube with a layer of 5 c.c. of freshly prepared sulphuretted hydrogen water; no coloration or yellow ring should appear at the junction of the two solutions, even after the lapse of an hour. The test should be applied to both cold and hot solutions so as to detect arsenic acid; 0·000005 g. As in 1 g. acid can be detected, that is, $\frac{1}{20}$ mg. As in the quantity taken for the test.

(*b*) According to the German Pharmacopœia, III., 1 c.c. of hydrochloric acid is treated with 3 c.c. of stannous chloride solution, prepared by rubbing to a cream five parts of crystallised stannous chloride and one part of hydrochloric acid, saturating with dry hydrochloric acid gas, and filtering. No coloration should appear after the mixed solutions have stood for one hour.

(*c*) Hager's Kramato-method[2] is extremely sensitive, and quickly and simply carried out. One c.c. of the hydrochloric acid is diluted with 2 c.c. of water and a little ammonium oxalate added. A drop of the solution is then evaporated on a strip of brass (previously rubbed

[1] *Chem. Zeit.*, 1894, 18, 225. [2] *Pharm. Centr.*, 1884, 265.

clean with sand and water and dried), the heating being so regulated that no ammonium salts are volatilised. If arsenic be present, a stain is produced varying from grey through red to black, according to the quantity of arsenic in the acid.

(*d*) A delicate method for the detection of arsenic has been described by Schlickum.[1] If a minute crystal (0·01 to 0·02 g.) of sodium sulphite is added to a solution of 0·3 to 0·4 g. stannous chloride in 3 to 4 g. of hydrochloric acid, both sulphur dioxide and sulphuretted hydrogen are evolved, the latter being due to the reducing action of the stannous chloride on the sulphurous acid. If hydrochloric acid containing arsenic be carefully introduced so as to form a layer on the top of the solution, a yellow ring of arsenious sulphide immediately forms at the zone of contact. The reaction is given by $\frac{1}{20}$ mg. of arsenious acid. The ring gradually extends in an upward direction, and in the presence of $\frac{1}{2}$ mg. of arsenious acid the whole of the acid layer assumes a yellow colour in the course of a few minutes. The reaction proceeds more slowly when the arsenic is present in the arsenic condition. The success of this test depends on the use of a minimum quantity of sodium sulphite and of strong hydrochloric acid, so as to prevent the separation of stannous sulphide.

(*e*) Gutzeit's test (p. 445) is extremely delicate and allows the detection of $\frac{1}{1000}$ mg. As_2O_3, but it involves the careful observation of the conditions referred to in connection with sulphuric acid, since sulphuretted hydrogen, hydrogen phosphide, and antimoniuretted hydrogen affect both silver nitrate and mercuric chloride papers in a similar manner to arseniuretted hydrogen.

Quantitative determination of Arsenic.—The arsenic present in ordinary, non-purified, commercial hydrochloric acid, may be determined quantitatively either by reducing 20 g. of the acid with sulphurous acid, driving off the excess of the latter, neutralising with sodium carbonate, and titrating with iodine; or by precipitating with sulphuretted hydrogen, and weighing the sulphide obtained after extraction with carbon bisulphide. Neither method is free from objection, and in the latter case it is difficult to be certain that the arsenic is actually present as pure As_2S_3. Kretzschmar[2] therefore recommends the following method:—

The highly diluted acid is nearly neutralised by addition of sodium carbonate, ammonia and yellow ammonium sulphide then added, followed by chemically pure hydrochloric acid in excess, and a strong current of sulphuretted hydrogen passed for two hours through the solution, which is kept hot on the water-bath. By this treatment the precipitation, which otherwise requires from fifteen to twenty-four hours, is complete in the time stated. The precipitate of arsenious

[1] *Analyst*, 1886, 11, 19. [2] *Chem. Zeit.*, 1891, 15, 269.

sulphide is washed, dissolved in potassium hydroxide with addition of bromine, and the arsenic finally precipitated in slightly acid solution by ammonia and magnesia mixture and weighed as magnesium pyro-arsenate. This method may also lead to erroneous results; should the ignition be too strong, arsenic may be distilled off, whilst if too gentle, the conversion to the pyroarsenate is likely to be incomplete.[1] The arsenic may also be determined volumetrically, by boiling the sulphide with a few c.c. of concentrated sulphuric acid till it is completely dissolved and all sulphur dioxide is expelled, cooling, diluting, nearly neutralising with sodium hydroxide, adding excess of sodium bicarbonate, and titrating with $N/10$ iodine solution.

4. *Iron.** Five g. diluted to 25 c.c. should yield no coloration on the addition of a few drops of potassium thiocyanate solution.

For detecting traces of iron in strong acids, Venable[2] recommends making use of the blue solution obtained on treating cobaltous nitrate with strong hydrochloric acid. Traces of ferrous salts change the blue colour of such a solution to green; ferric salts are without effect.

For quantitative work the iron is reduced with zinc, the solution diluted with a large volume of distilled water, a 20 per cent. solution of manganese sulphate, free from iron, added, and the whole titrated with $N/20$ potassium permanganate solution (1·5803 g. per litre), of which 1 c.c. = 0·002792 g. Fe. A blank experiment on an equal volume of the distilled water, as used above, is made at the same time and the volume of permanganate solution necessary to produce a faint permanent rose tint deducted. Traces of iron are determined colorimetrically as described above (p. 453).

5. *Sulphurous acid.* According to Krauch, the addition of a few c.c. of the diluted acid should not destroy the faint blue colour of water to which a little iodine and starch solution have been added. In the absence of chlorine and ferric chloride, sulphurous acid may also be detected by means of sulphuretted hydrogen (white cloudiness due to separated sulphur) or by stannous chloride (brown precipitate of stannous sulphide). For quantitative work, titration with permanganate or iodine solution is adopted. It is, however, safer to estimate the total sulphuric acid present after oxidation by the above reagents, or by hydrogen peroxide, and to deduct from this the sulphuric acid originally present as found under 2.

6. *Simultaneous examination for Sulphurous and Arsenious acids.* If on adding iodine solution to the acid the iodine is decolorised, at least one of these impurities is present.

Should this be the case, Hilger[3] recommends the addition of more iodine solution till an excess is present; the acid is then transferred to

[1] *Cf.* Blattner and Brasseur, *Chem. Zeit.*, 1904, **28**, 211.
[2] *Z. anal. Chem.*, 1889, **28**, 699.
[3] *Jahresber. d. chem. Tech.*, 1875, p. 445.

a test tube and a few pieces of zinc added. The test tube is loosely stoppered by a cork carrying a piece of silver nitrate paper; arsenic, if present, produces a darkening of the paper, owing to the arseniuretted hydrogen evolved. Should no darkening occur, the original acid is tested for sulphurous acid by first precipitating the sulphuric acid by means of barium chloride and adding iodine solution to the filtrate till a coloration is produced; should sulphurous acid be present in the original hydrochloric acid, a further precipitation of barium sulphate will take place.

7. *Chlorine.* No blue coloration should result when 1 c.c. of the acid, diluted with water, is added to 5 c.c. of very dilute freshly prepared starch solution to which a few drops of potassium iodide solution and a few drops of dilute sulphuric acid have been added. By carrying out the test in this manner any blue coloration due to the presence of iodate in the potassium iodide would appear before the addition of the hydrochloric acid to be tested. An alternative method of testing is to shake the acid in a closed flask with a perfectly clean, bright piece of thin copper foil, first displacing the air in the flask by carbon dioxide; should chlorine be present, part of the copper goes into solution and may be detected by potassium ferrocyanide, etc. For ordinary purposes it is sufficient to hold a piece of iodised starch paper in the vapours given off from the warmed acid; an immediate blue coloration shows the presence of free chlorine.

8. *Selenium* is detected by the Reinsch test and gives a similar stain on copper to that produced by arsenic; on heating the copper foil in a dry test tube a sublimate is obtained which dissolves in sulphuric acid with the formation of a brownish-green coloration.[1]

According to Reidemeister,[2] reddish-brown deposits of selenium are sometimes found in roaster acid but never in pan acid.

9. *Determination of Hydrochloric acid.* Ten c.c. of the acid, the specific gravity of which has been previously determined, is measured from an accurate pipette, diluted to 200 c.c. with water, and 10 c.c. of this solution taken for the test; or about 1 g. of the acid is accurately weighed in the bulb-tap pipette (Fig. 201, p. 463), allowed to flow into water, and the whole of the solution so obtained taken for titration. The diluted solution is treated with sodium carbonate, free from chloride, until the reaction is neutral or very faintly alkaline. This may be done rapidly and without appreciable loss of acid by spirting, if sodium carbonate solution corresponding to the acid content, as determined from the specific gravity by the aid of the table given above (p. 517), be added from a burette. A little neutral potassium chromate solution is then added and the solution titrated with $N/10$ silver nitrate solution until a distinct faint rose

[1] Drinkwater, *Jahresber. d. chem. Tech.*, 1884, p. 348.

[2] Cumming, *Hydrochloric Acid and Saltcake*, 1913, p. 72.

coloration, which remains permanent on stirring, is produced (*cf.* p. 73). From the volume required, the usual deduction of the 0·2 c.c. necessary to produce the coloration must be made. The percentage of HCl in the acid is obtained by multiplying the number of the remaining c.c. by 0·7292 and dividing by the specific gravity of the acid.

The titration may also be carried out by Volhard's method (p. 74).

Should metallic chlorides be present, the above method will obviously lead to incorrect results; but appreciable quantities of such chlorides seldom occur. In such samples the total acidity is determined, the sulphuric acid estimated as in 2, and deducted from the total acidity. This method may be employed, of course, even in the absence of metallic chlorides.

LITERATURE

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THE MANUFACTURE OF SODIUM CARBONATE

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I. THE LEBLANC SODA PROCESS

RAW MATERIALS

1. SALTCAKE

THE analytical examination of saltcake has already been described (p. 509 *et seq.*).

2. CALCIUM CARBONATE

This is employed in the form of limestone, chalk, or dried lime-mud, obtained either from the Chance process (see under "Soda Residues") or from the causticising pans where the lime process is used.

The analysis is generally confined to the determination of moisture, matter insoluble in hydrochloric acid, calcium, and, where necessary, magnesium. Full details are given under the manufacture of "Bleaching powder" (p. 581).

3. MIXING SLACK

As a rule, coal is employed for the black ash mixture; occasionally, however, lignite, wood, charcoal, coke, etc., are used. In taking the samples for analysis, the rules given on pp. 4 and 327 must be rigorously observed. The coal is usually examined for moisture, non-volatile matter, ash, sulphur, and nitrogen. The methods of analysis are described in the section on "Fuel" (pp. 327-357).

CONTROL OF WORKING CONDITIONS

1. BLACK ASH

The black ash is tested daily for its percentage of free and total lime, and for sulphide, sulphate, and carbonate of sodium; and at less frequent intervals for sodium hydroxide and chloride. The deter-

mination of the free lime is important, since it aids the lixiviation by the disruptive action brought about by hydration, and unless a certain quantity be present in the ball the lixiviation process proceeds very slowly and may be very incomplete. The sodium found as Na_2CO_3, Na_2S, and NaOH is calculated to Na_2SO_4, and the value obtained added to that of the Na_2SO_4 present as such, giving the total sodium expressed as Na_2SO_4. By comparing this value with the figure found for "total lime," it is possible to ascertain from the analysis whether the correct proportion of saltcake and lime has been used in the mixing.

The determination of the various constituents is carried out as follows.[1] Fifty g. of the average sample is rapidly, but thoroughly, ground in a mortar (in works it is often possible to employ some mechanical contrivance for this purpose), and introduced into a 500 c.c. flask. Lukewarm distilled water, freed from carbonic acid by previous boiling, is then poured on the mass, which is thoroughly shaken at once, and subsequently at intervals during two hours. It is important that the mixture should be thoroughly shaken at the start, otherwise the mass cakes to a solid block on the bottom of the flask and cannot then be broken up.

FIG. 205.

1. **Free Lime.**—At the end of the two hours the flask is filled up to the 500 c.c. mark, and two portions, each of 5 c.c., of the thoroughly mixed contents are taken for the estimation of free and total lime. For this purpose it is advisable to use a pipette, the outlet of which terminates abruptly, as shown in Fig. 205, instead of an ordinary pipette, the long narrow outlet tube of which is very apt to get blocked by the solid matter present.

The frothy material on the outside of the pipette is washed off by means of a wash-bottle, the contents emptied into a beaker and the pipette washed out with water. An excess of barium chloride solution and a drop of phenolphthalein solution are added, and the mixture titrated with $N/5$ hydrochloric acid until the red coloration just vanishes. Each 1 c.c. of the acid = 0·00561 g. CaO. Provided the shaking is efficient, concordant results are obtained.

2. **Total Lime.**—This determination is carried out by first converting the lime into calcium chloride and then into calcium carbonate, in neutral solution, by addition of an excess of $N/5$ sodium carbonate solution, the excess of this reagent being titrated back by $N/5$ acid. Five c.c. of the thoroughly shaken solution, as used under 1, is treated in a small Erlenmeyer flask with a few c.c. of strong hydrochloric acid and then heated to boiling until all gas has been expelled. A drop of

[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 601; *Z. angew. Chem.*, 1890, 3, 570.

methyl orange is added to the cooled solution, which is then exactly neutralised with sodium carbonate solution; 30 to 40 c.c. of $N/5$ sodium carbonate is next added and the solution again heated to boiling. By this treatment the whole of the calcium is precipitated as calcium carbonate, together with a certain quantity of oxide of iron, alumina, and magnesia, but the quantity of the three latter compounds is small and for the present purpose may be neglected. The mixture is transferred to a 200 c.c. flask, the flask filled to the mark with water, and the excess of sodium carbonate determined by titrating 100 c.c. of the filtered solution with $N/5$ hydrochloric acid, using methyl orange as indicator.

If the number of c.c. of acid required = n, and 30 c.c. of sodium carbonate solution have been taken, the total calcium expressed as CaO is = $(30-2n)\times 0{\cdot}00561$, or, expressed as $CaCO_3$, = $(30-2n)\times 0{\cdot}01001$.

The results obtained by these two tests are only approximate, owing to the impossibility of obtaining a really average sample; they serve, however, as a guide, provided that they are made on the thoroughly mixed turbid solution. The same reservation holds for all the results obtained for black ash, and on this account it is important to take the physical appearance of the ball into consideration.

After the portions for the above tests have been taken, the 500 c.c. flask is well stoppered and allowed to stand until the solution has become perfectly clear, after which portions are withdrawn for the following determinations.

3. **Total available Alkali.**—Ten c.c., = 1 g. of black ash, is titrated cold with hydrochloric and methyl orange. This gives the total alkalinity, and is a measure of the Na_2CO_3, NaOH, and Na_2S. The quantity of Na_2CO_3 present is found by deducting the values found under 4 and 5 and is equal to 0·053 g. for each 1 c.c. of normal acid. Any error due to small amounts of alumina and silica may be neglected.

4. **Caustic Soda** is determined by adding an excess of barium chloride solution (10 c.c. of a 10 per cent. solution of $BaCl_2 . 2H_2O$ will more than suffice) to 20 c.c. of the liquor contained in a 100 c.c. flask, filling to the mark with boiling water, shaking and corking; the precipitate settles well, the solution becoming clear after a few minutes standing. Fifty c.c. of the clear solution is pipetted off and titrated when cold with hydrochloric acid and methyl orange. The solution should not be filtered, because filter paper absorbs appreciable quantities of barium salts. A simpler and more exact method is to titrate the solution (10 c.c.) in presence of the precipitate, employing phenolphthalein as indicator, the colour change taking place when all alkali hydroxide is neutralised. Each 1 c.c. of acid corresponds to 0·04001 g. NaOH in 1 g., the weight of black ash taken. In this method any sodium sulphide present is estimated as hydroxide; silica is present in

such extremely minute quantity that it does not interfere with the determination, though it may do so in the finished caustic soda (*cf.* p. 566).

5. **Sodium sulphide.**—Ten c.c. of the solution is diluted to about 200 c.c. with boiled air-free water, acidified with acetic acid and titrated quickly with iodine solution, employing starch solution as indicator. If *N*/10 iodine solution be used (12·692 g. I per litre), each 1 c.c. = 0·003903 g. Na_2S; if the solution be made up to contain 3·252 g. I per litre, then each 1 c.c. = 0·001 g. Na_2S. The more exact process, due to Lestelle, described under the analysis of the finished soda ash, is unnecessary in testing black ash. A detailed investigation has been made by Marchlewski[1] on the estimation of sulphide-sulphur.

No account need be taken of other sulphur compounds, with the exception of sulphate; their separation is dealt with under Soda Mother Liquors (p. 531).

6. **Sodium chloride.**—Ten c.c. of the solution is neutralised as exactly as possible with nitric acid, most conveniently by adding the same number of c.c. of normal nitric acid (63·02 g. HNO_3 per litre) as were required of hydrochloric acid in test 3. The solution is then boiled until all sulphuretted hydrogen has been driven off, filtered from separated sulphur and, after the addition of a little neutral potassium chromate solution, titrated with silver nitrate solution. Or nitric acid of any convenient strength may be added in excess and the solution rendered slightly alkaline by addition of sodium carbonate or bicarbonate after all the sulphuretted hydrogen has been expelled. Volhard's method, using ammonium thiocyanate as indicator (p. 74), can also be employed, in which case it is not necessary to neutralise the excess of nitric acid. Each 1 c.c. of *N*/10 silver nitrate solution corresponds to 0·005846 g. NaCl; a solution containing 2·9061 g. $AgNO_3$ per litre corresponds per 1 c.c. to 0·001 g. NaCl.

7. **Sodium sulphate.**—Twenty c.c. of the solution is acidified with hydrochloric acid, in not too great excess, heated to boiling, and a hot solution of barium chloride added. Should the bulk of precipitated barium sulphate be small, it may be at once transferred to and washed on the filter with hot water and ignited in a platinum crucible whilst still wet. Each one part $BaSO_4$ corresponds to 0·6085 parts Na_2SO_4.

2. Vat Liquor

Specific gravity.—The specific gravity is taken by the hydrometer, and necessarily in the warm solution, since crystals separate on cooling. Lunge[2] has shown that if the temperature of the liquor be taken at the same time a very close approximation to the amount

[1] *Z. anal. Chem.*, 1893, 32, 405.

[2] *Chem. Ind.*, 1881, 4, 376.

of solid material in the liquor may be obtained since the percentage corresponds almost exactly with the percentage of pure sodium carbonate present in a sodium carbonate solution of the same specific gravity (*cf.* Tables, pp. 549 and 550).

The chemical examination of the vat liquor includes the following determinations. It is best, and saves much time, to withdraw small portions (2 to 5 c.c.) in accurate pipettes from the non-diluted liquor for the tests.

1. **Sodium carbonate.**—Two c.c. is titrated with normal hydrochloric acid. If methyl orange be employed as indicator, the solution is cooled by addition of cold water. The number of c.c. found under 2, together with $\frac{1}{10}$ of the number of c.c. found under 3, must be deducted from the volume required in this test.

2. **Caustic Soda.**—Two or 5 c.c. is measured off and treated as described on p. 526.

3. **Sodium sulphide.**—This is determined in 2 c.c. of the liquor as described on p. 527. Errors arising from the presence of other sulphur compounds may be neglected.

4. **Sodium sulphate.**—Two c.c. is examined as on p. 527.

5. **Total Sulphur.**—Five c.c. of the liquor is oxidised by addition of strong bleaching powder solution and hydrochloric acid in excess, taking care that the solution smells strongly of chlorine. The solution is filtered and precipitated by barium chloride.

6. **Sodium chloride.**—Two or 5 c.c. is neutralised as described on p. 527, and titrated.

7. **Sodium ferrocyanide**—This may be determined by de Haën's permanganate method, viz., precipitation as Prussian blue, decomposition of this on the filter by sodium hydroxide solution, and titration of the re-formed sodium ferrocyanide by permanganate. The following modification of Hurter's copper sulphate method is, however, both better and quicker. In its original form[1] the method had disadvantages which Lunge and Schäppi[2] have overcome by adding only so much bleach solution as is actually necessary for the oxidation. The improved method is carried out as follows. Twenty c.c. of the liquor, or more in the case of a low cyanide content, is acidified with hydrochloric acid and a strong solution of bleaching powder added from a burette to the well-agitated liquor. A drop of the mixture is withdrawn from time to time and added to a drop of ferric chloride, free from ferrous chloride, on a white plate. The oxidation of ferrocyanide to ferricyanide is complete when the ferric chloride test gives only a brown solution free from Berlin blue. A drop of bleaching powder in excess does not matter, but if too much has been taken or too large a volume of the

[1] *Chem. News*, 1879, **39**, 25; Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 672.
[2] *Chem. Ind.*, 1881, **4**, 370.

solution withdrawn for spotting, a fresh portion of the sample is taken and nearly the full quantity of bleach solution required run in at once, only a few tests on the plate being then necessary.

N/10 copper solution (containing 3·178 g. Cu or 12·486 g. crystallised copper sulphate per litre) is then added from a burette to the oxidised liquor, causing precipitation of yellow copper ferricyanide $Cu_3Fe_3(CN)_{12}$. From time to time the solution is tested by mixing a drop of the turbid liquid with a drop of dilute ferrous sulphate solution on a porcelain plate. The addition of the copper solution is continued as long as the test gives the blue colour, due to the interaction of the ferrous sulphate and sodium ferricyanide, and until the colour produced on the plate has a distinct reddish tinge. When this stage has been reached all the ferricyanide has been converted into the copper compound ; the red colour is due to the reduction of the yellow ferricyanide of copper to the red ferrocyanide by the ferrous sulphate. The reaction is finished as soon as the first marked reddening occurs, even though this disappears after a short time. Each 1 c.c. of the copper solution should correspond to 0·01013 g. $Na_4Fe(CN)_6$; but later work[1] has shown that such is not the case, and that the actual quantity is 0·0123 g. It is, however, advisable to standardise the copper solution directly with pure potassium ferrocyanide.

Zulkowsky[2] determines the ferrocyanide by adding the liquor to a boiling solution of zinc sulphate, acidified with sulphuric acid, until a blue colour is produced at the line of contact when a drop of the solution and a drop of ferric chloride are placed a little distance apart on filter paper. The precipitate has the composition :—

$$K_4Fe(CN)_6 \cdot 3Zn_2Fe(CN)_6 \cdot 12H_2O.$$

Zaloziecki[3] adds zinc carbonate to the solution to be tested, passes carbon dioxide through the hot solution, and titrates a portion of the filtrate with normal acid and methyl orange. The ferrocyanide present in the liquor is calculated from the quantity of sodium carbonate formed according to the equation :—

$$2Na_4Fe(CN)_6 + 4ZnCO_3 = 2Zn_2Fe(CN)_6 + 4Na_2CO_3.$$

Should the liquor, as in the case of vat liquor, be alkaline before the addition of the zinc carbonate, the acid corresponding to such alkalinity must be deducted from that used after the above treatment.

The *thiocyanate* may be determined approximately by Hurter's method, which consists in first precipitating the ferrocyanide by addition of zinc chloride to the acidified liquor, filtering, and then comparing the red coloration, produced on addition of ferric chloride to the filtrate, with

[1] *Chem. Ind.*, 1882, **5**, 79.
[2] *Dingl. polyt. J.*, 1883, **249**, 168.
[3] *Z. angew. Chem.*, 1890, **3**, 210 and 301.

a series of standard solutions containing known quantities of thiocyanate and ferric chloride. See also pp. 630 and 642.

8. Silica, Alumina, and Ferric oxide. Parnell's method.[1]—One hundred c.c. of the liquor is treated with an excess of hydrochloric acid, a considerable quantity of ammonium chloride solution added, followed by excess of ammonia, and the solution boiled until all smell of ammonia has disappeared. The precipitate settles well, and may be filtered and washed without difficulty. On washing with hot water it acquires a deep blue colour (owing to formation of Prussian blue ?). The mixture of SiO_2, Al_2O_3, and Fe_2O_3 is ignited and weighed.

9. Carbonating Test.—A considerable volume of the vat liquor is carbonated by passing a current of carbon dioxide through it, and filtered. The filtrate is evaporated to dryness and the residue tested for alkalinity, sodium sulphate, and sodium chloride.

An example of the method of calculating the results and of the practical conclusions to be drawn from the data obtained, is given in Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 674.

3. Carbonated Liquors

These are examined in the same way as vat liquor. The contained *bicarbonate* is determined in addition. The determination of carbonic acid is performed most accurately and quickly by the Lunge and Marchlewski method as modified by Lunge and Rittener[2] (p. 615), which is equally applicable for very large and for very small amounts of carbonic acid. Failing the apparatus necessary for this method, approximate results, sufficiently accurate for all practical purposes, may be obtained as follows.

The carbonated liquor is titrated after cooling to nearly 0°, using phenolphthalein as indicator with $N/5$ hydrochloric acid until the red colour disappears. The other conditions, high concentration and a large percentage of sodium chloride, are present at the start and are brought about during the titration respectively. Methyl orange is then added and the titration continued until the change to pink occurs. If a c.c. of $N/5$ hydrochloric acid has been taken for the first titration, and b c.c. for the second, then the number of c.c. corresponding to the constituents of the liquor are: $b-a$ for the bicarbonate, $2a$ for the alkali present as Na_2CO_3, and $a+b$ for the total alkali. The ratio of bicarbonate to carbonate can thus be readily calculated.

Other methods for determining bicarbonate are described under "Bicarbonate" (p. 569).

The mother liquors resulting from the manufacture of soda crystals are examined in the same way as carbonated liquors.

[1] *Chem. Ind.*, 1880, 3, 242. [2] *Z. angew. Chem.*, 1906, 19, 1849.

4. SODA MOTHER LIQUORS

Appreciable quantities of sodium sulphite and thiosulphate may occur in these liquors, in addition to sodium sulphide, especially when they are derived from non-carbonated liquors.

The estimation of sulphide-sulphur is generally carried out by expelling the sulphuretted hydrogen with acid and absorbing it by a suitable reagent. The detailed communications of Marchlewski[1] and of Jannasch[2] give full information on this method.

The determination is best made in a flask provided with a tap-funnel reaching nearly to the bottom, and with an exit-tube connected with one or two ten-bulb tubes (Fig. 193), filled with ammoniacal hydrogen peroxide, either free from sulphuric acid or in which the quantity of sulphuric acid present is known. The material is introduced into the flask; in the case of a solid it is covered with well-boiled water, and after the air has been expelled from the apparatus by a rapid current of hydrogen, hydrochloric acid, diluted with an equal volume of well-boiled water, is slowly admitted through the funnel. The solution is finally raised to gentle boiling, and hydrogen passed through for fifteen minutes. The contents of the receiving tubes are then heated to boiling to complete the oxidation, acidified with hydrochloric acid, and the sulphur precipitated as barium sulphate. Sodium hydroxide solution, free from sulphate, may be employed instead of the ammoniacal hydrogen peroxide, and the absorbed sulphur gases converted to sulphate by treating the solution with hydrochloric acid and bromine water and boiling until the excess of bromine has been expelled. The hydrogen employed must be washed with an alkaline solution of lead acetate and then with water.

Instead of the above absorbents $N/10$ iodine solution may be employed, the first bulb-tube being filled with this solution, and the second with an equal volume of $N/10$ sodium thiosulphate solution, to catch any iodine carried forward. The two solutions are combined at the end of the experiment, and the excess of thiosulphate determined by titration. The sulphuretted hydrogen corresponding to the iodine taken up is calculated from the equation :—

$$H_2S + I_2 = 2HI + S.$$

The presence of carbonate in the liquors does not interfere in any of these methods, but sulphites and thiosulphates will lead to error owing to the liberation of sulphur dioxide.

The following method[3] is well adapted to the rapid determination

[1] *Z. anal. Chem.*, 1893, **32**, 403.
[2] *Z. anorg. Chem.*, 1896, **12**, 124, 134, 158.
[3] Grossmann, *Chem. News*, 1878, **37**, 224; *Z. anal. Chem.*, 1879, **18**, 79.

of *sulphide*, *sulphate*, *sulphite*, and *thiosulphate*, when present together in solution.

1. The sulphate originally present is determined in one portion of the liquor. The air in the flask used for precipitation is first displaced by carbon dioxide, to prevent oxidation of the lower sulphur compounds present, the solution heated to boiling, acidified with hydrochloric acid, and the sulphate precipitated by addition of barium chloride.

2. A second portion is acidified with acetic acid, diluted with air-free water, and titrated with iodine, using starch as indicator. This gives the $Na_2S + Na_2SO_3 + Na_2S_2O_3$.

3. A third portion is treated with cadmium carbonate to remove the sulphide, filtered, the filtrate acidified with acetic acid and titrated with iodine. This gives the Na_2SO_3 and $Na_2S_2O_3$ present. The difference between the readings obtained under 2 and 3 gives the Na_2S.

4. A fourth portion is oxidised by bromine water or bleaching powder solution (p. 528), and the total sulphate estimated. From the value so obtained, the sulphate found under 1 and the sulphate corresponding to the sulphide present are deducted. If B represents the remaining sulphate, expressed in g. Na_2SO_4, and derived from the sulphite and thiosulphate, and A the total sulphite and thiosulphate found in test 3, expressed in g. of iodine, the $Na_2S_2O_3$ present = (0·741784B − 0·414698A) g. and the Na_2SO_3 = (0·661417A − 0·295775) g.

Kalmann and Spüller[1] give the following process based on the behaviour of barium sulphite and barium thiosulphate towards water, the former being practically insoluble, whilst the latter is soluble in a large volume of water.

(*a*) The total alkalinity is determined in a measured volume of the solution by titration with normal acid, using methyl orange as indicator. The acid required corresponds to the sum of the sodium carbonate, sodium sulphide, sodium hydroxide, and half of the sodium sulphite present.

(*b*) An equal volume of the liquor is acidified with dilute acetic acid and titrated with *N*/10 iodine after the addition of starch solution. The iodine used corresponds to the sum of the sodium sulphide, sodium sulphite, and sodium thiosulphate present.

(*c*) A portion of the solution, double the volume of that employed in test 1, is treated with an alkaline zincate solution to precipitate the sulphide, and made up to a definite volume. One-half of this is then filtered off, acidified with acetic acid, and titrated with *N*/10 iodine solution and starch. The iodine used corresponds to the sodium sulphite and sodium thiosulphate.

(*d*) Excess of barium chloride is added to a larger portion of the

[1] *Dingl. polyt. J.*, 1887, **264**, 456.

liquor—three or four times that used in test 1—the solution made up to a definite volume with well-boiled water, the precipitate allowed to settle, and the solution then filtered.

(α) One-third or one-quarter of this solution is titrated with normal acid, the volume required corresponding to the sodium hydroxide and sulphide present.

(β) A second one-third, or one-quarter, is acidified with acetic acid and titrated with $N/10$ iodine solution. This gives the sulphide and thiosulphate present.

The calculation is as follows:—

$b - d\beta$ = A c.c.	$N/10$ iodine solution,	corresponding to the	Na_2SO_3
$b - c$ = B ,,	,,	,,	Na_2S
$d\beta - (b - c)$ = C ,,	,,	,,	$Na_2S_2O_3$
$d\alpha - 1/10$ B = D ,,	normal acid,	,,	NaOH
$a - (d\alpha - 1/20$ A) = E ,,	,,	,,	Na_2CO_3.

The following method for the determination of sulphite and thiosulphate, when present together, is due to Kalmann.[1] In the reaction $Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$, acid is produced; in the reaction $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, the solution remains neutral. The test is therefore carried out by allowing the solution to be examined to flow from a burette into a measured volume of iodine solution until this is just decolorised, then adding methyl orange and titrating the acid formed in the iodine titration by $N/10$ sodium hydroxide solution. The iodine equivalent of the sodium hydroxide used gives the sulphite, and the difference between this and the total iodine taken corresponds to the thiosulphate. This method of testing is, of course, only applicable in the absence of carbonate or after any carbonate present has been exactly neutralised, which is not always easily accomplished.

Dobriner and Schranz[2] state that only Na_2S and NaSH, or Na_2S and NaOH, and not all three substances, can exist together in solution, and that this should be taken into account in calculating and stating the results of analysis.

Autenrieth and Windaus[3] separate sulphite and thiosulphate by addition of strontium nitrate, which precipitates the sulphite but leaves the thiosulphate in solution. According to experiments carried out in Lunge's laboratory by Bruhns, the method gives useful if not quite accurate results, and it may therefore be recommended, more especially as it affords a direct separation of the two substances.

Feld[4] describes the following process for estimating sulphur in all stages of oxidation, the method being more particularly intended for liquors containing compounds of the alkali earths. Free sulphur, which

[1] *Ber.*, 1887, **20**, 568.
[2] *Z. angew. Chem.*, 1896, **9**, 455.
[3] *Z. anal. Chem.*, 1898, **37**, 291.
[4] *Chem. Ind.*, 1898, **21**, 372.

may be dissolved in the thiosulphate or polysulphide present in the liquors, is extracted by carbon disulphide and separated from the solvent by distillation. The sulphuretted hydrogen is then driven off by distilling the liquor with magnesium chloride in a current of carbon dioxide (which makes the reaction quantitative) and collected in $N/10$ iodine solution. For this test three absorption vessels are employed; two filled with iodine solution, and the third with $N/10$ thiosulphate solution to retain any iodine carried forward by the gas. The sulphuretted hydrogen liberated may arise from monosulphide, polysulphide, or sulphydrate. Should polysulphide be present, sulphur separates out during the distillation with magnesium chloride, and is subsequently extracted from the residue by means of carbon bisulphide; should sulphite also be present, a portion of the polysulphide sulphur may combine with this to form thiosulphate. The residual liquor from the distillation is oxidised by the addition of iodine in excess, which liberates sulphur from any sulphide of iron present, according to the equation :—

$$2FeS + 3H_2O + 6I = Fe_2O_3 + 2S + 6HI.$$

The liberated sulphur is extracted with carbon bisulphide as before. The thiosulphate, or rather the resulting tetrathionate, is decomposed by distilling the residue from the previous operation, or from a fresh portion oxidised by iodine, with aluminium and hydrochloric acid, and collecting the sulphuretted hydrogen evolved in iodine solution, as above. The conversion of the tetrathionate to sulphuretted hydrogen is quantitative, but additional sulphuretted hydrogen will, of course, be produced from any other polythionates present. Sulphurous acid is determined by treatment with excess of mercuric chloride, which decomposes all the sulphur compounds with the exception of sulphite, followed by distillation with hydrochloric acid, and collecting the liberated sulphur dioxide in iodine solution.

The following method has been worked out by Lunge and J. H. Smith.[1] The sulphate is determined by displacing the air in the precipitating flask by carbon dioxide to prevent oxidation, heating the solution, acidifying with hydrochloric acid, and precipitating with barium chloride. A second portion is diluted with air-free water acidified with acetic acid, and titrated with $N/10$ iodine solution, running the acidified solution from a burette into a measured volume of iodine solution until the iodine is decolorised, or running a measured volume from a pipette into excess of iodine and determining the excess by titration with thiosulphate. A third portion, four times as large, is treated with zinc acetate or cadmium carbonate to remove the sulphide, made up to a definite volume, allowed to settle, and

[1] *Chem. Ind.*, 1883, **6**, 301.

one quarter of the solution titrated with iodine as above, whilst a second quarter is allowed to flow into a considerable excess of neutral permanganate solution; an acid solution of ferrous sulphate of known value in terms of the permanganate solution then added, and the excess of this finally titrated back with permanganate. If W be the weight of sulphur as thiosulphate oxidised to sulphate by 1 c.c. of the permanganate solution (according to the equation $3Na_2S_2O_3 + 8KMnO_4 + H_2O = 3Na_2SO_4 + 3K_2SO_4 + 8MnO_2 + 2KOH$), then 2W is the weight of sulphur as sulphite similarly oxidised; and if W′ be the weight of sulphur as thiosulphate converted into tetrathionate by 1 c.c. of iodine solution, then W′/4 is the weight of sulphur as sulphite similarly converted into sulphate. If then a given volume of the solution required V c.c. of permanganate solution, and an equal volume required V′ c.c. of iodine solution, the sulphur as thiosulphate is given by $1/7\,(8WV - W'V')$, and that as sulphite by $2/7\,(W'V' - WV)$.

The quantity of sulphide present is found by deducting the value V′ from the figure for the original iodine titration.

This process has been further tested by Lunge and Segaller[1] and found to give exactly the same results as are obtained by the method proposed by Richardson and Aykroyd,[2] who had, through incorrect manipulation, stated that the Lunge-Smith method was inexact. Richardson and Aykroyd determine the sulphate by precipitating cold with barium chloride after addition of tartaric acid; a second portion is treated with iodine, and the acid produced by interaction with the sulphite titrated with methyl orange as indicator, exactly as described by Kalmann (p. 532). The sulphide-sulphur is determined in the ordinary manner.

A very complete summary of the numerous earlier investigations on the action of potassium permanganate on thiosulphate, supplemented by further experiments, has been made by Dobbin,[3] from which he has drawn the following conclusions. When neutral solutions of thiosulphate and permanganate react in the cold, there results a dark brown, flocculent precipitate of variable composition, the solution remaining neutral. The quantity of permanganate necessary to produce a permanent coloration is less than that indicated by theory, assuming the thiosulphate to be oxidised to sulphate, and the permanganate to be reduced to manganese dioxide. The brown precipitate always contains manganese in lower stages of oxidation than MnO_2, in varying quantity, together with traces of sulphur compounds. The solution separated from this precipitate always contains tetrathionate in addition to sulphate, and complete oxidation to sulphate cannot be effected even after prolonged boiling; other sulphur compounds do not appear to be present.

[1] *J. Soc. Chem. Ind.*, 1900, **19**, 221. [2] *Ibid.*, 1896, **15**, 171.
[3] *J. Soc. Chem. Ind.*, 1901, **20**, 212.

In view of these results, it would appear that the accuracy of all the earlier methods for the separation of the various sulphur compounds must be called into question.

Dobbin confirms the statement, frequently lost sight of, that barium sulphate is not altogether insoluble in the presence of thiosulphate, so that when thiosulphate is present the sulphate determination is inexact.

Sander[1] determines thiosulphate in presence of sulphide, by first finding the sum of the two by titration with iodine, then adding to another portion excess of mercuric chloride, shaking till the dark precipitate has become white, adding ammonium chloride, and titrating the acid formed by means of $N/10$ soda and methyl orange. The reactions with mercuric chloride are

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O = 4HCl + 2Na_2SO_4 + 2HgS . HgCl_2$$
$$2Na_2S + 3HgCl_2 = 4NaCl + 2HgS . HgCl_2.$$

From the alkali consumed, the iodine equivalent of the thiosulphate is calculated, and subtraction of this from the total iodine used gives that equivalent to the sulphide. Sulphites and thiosulphates together can be determined by the same reaction, combining it with Bosshard and Grob's method.[2] The reactions of sulphites are

$$Na_2SO_3 + HCl = NaCl + NaHSO_3$$
$$NaHSO_3 + HgCl_2 = NaSO_3 . HgCl + HCl.$$

The sulphite is first determined by titration with hydrochloric acid and methyl orange, then excess of mercuric chloride is added, and the liberated acid titrated as above. Subtracting from the total acid that equivalent to the sulphite, the remainder is equivalent to the thiosulphate. If sulphide, sulphite, and thiosulphate be all present, they can be rapidly determined as follows:—1. 10 to 20 c.c. of the solution is run into a measured excess of $N/10$ iodine solution acidified with 5 to 10 c.c. (measured) of $N/10$ hydrochloric acid, and the excess iodine titrated with thiosulphate; this gives total sulphide, sulphite, and thiosulphate. 2. The solution is now titrated with $N/10$ caustic soda and methyl orange; subtracting the value of the acid added in 1 we get the value of the hydriodic acid liberated by the sulphite, and can calculate the iodine value of the sulphite. 3. The iodine value of the thiosulphate can now be found with mercuric chloride as above, and that of the sulphide is then obtained by subtraction.

The total sulphur and total oxidisable sulphur in soda mother liquors are also always determined (*cf.* p. 538).

[1] *Chem. Zeit.*, 1915, **39**, 945; *J. Soc. Chem. Ind.*, 1916, **35**, 307.

[2] *Chem. Zeit.*, 1913, **37**, 465; *J. Soc. Chem. Ind.*, 1913, **32**, 532. See also Wöber, *Chem. Zeit.*, 1920, **44**, 601.

5. Vat Waste

If it be not intended to recover the sulphur from vat waste, a determination of the available alkali is usually considered sufficient; a test of the total alkali is made in addition from time to time. If the sulphur is to be recovered, the further determinations of oxidisable and total sulphur must always be made, although different methods of testing may be adopted according to the nature of the process in use.

A. *The non-oxidised Alkali Waste.*

One or two representative samples are taken each day from the heaps of fresh waste, and placed in large, wide-necked, glass-stoppered bottles. If the samples be exposed to the atmosphere until dry, and determinations made on the air-dried waste, very variable results are obtained, according to the extent of oxidation undergone by the waste. Hence the waste is always examined in the moist condition and the results calculated on this basis. The percentage of water may be taken in round figures as 40; it is, however, determined directly when necessary.

1. **Available Soda.**—Watson's[1] modification of Lunge's method is generally employed.

Twenty g. of the waste is well stirred with from 150 to 200 c.c. of warm water and allowed to stand for one hour; at the end of this time the clear liquor is decanted off and treated for five minutes with a current of carbon dioxide. On passing the gas the solution becomes at first cloudy, but it clears later on as bicarbonate is formed and sulphuretted hydrogen evolved. This affords an indication that the whole of the calcium has been converted into bicarbonate. The solution is then evaporated to half its bulk or less, filtered from calcium carbonate, and the filtrate titrated with normal acid, using methyl orange as indicator. The filtrate still contains calcium compounds, but only in the form of sulphate or other neutral salt, which exerts no appreciable influence. Watson found by this method only 0·025 per cent. of soluble soda as an average of a series of analyses extending over a year.

2. **Total Soda** (including insoluble sodium compounds; Lunge's method).—17·71 g. of waste is heated in a porcelain or iron dish with sulphuric acid of sp. gr. 1·5 until the waste is thoroughly disintegrated and the mixture has been transformed into a stiff paste, when it is evaporated and all free sulphuric acid driven off by heating. Hot water is added to the residue, which is broken up with a wooden spatula and transferred to a 250 c.c. cylinder. Pure milk of lime (prepared from ordinary slaked lime by pouring off the first alkaline aqueous extract) is

[1] *J. Soc. Chem. Ind.*, 1890, **9**, 1107.

added to neutralise the free acid and precipitate any magnesia present, the cylinder filled to the 250 c.c. mark and the liquid allowed to settle. Fifty c.c. of the clear solution is pipetted off, treated with 10 c.c. of saturated barium hydroxide solution, filtered through a dry filter paper, and 50 c.c. of the filtrate treated with carbon dioxide till all the baryta is precipitated and, after filtration, titrated with normal acid. Each 1 c.c. of normal acid corresponds to 1 per cent. Na_2O when the above quantities are taken, this factor including allowance for the volume of the waste.

3. **Total Sulphur.**—Two g. of the waste is treated with excess of strong bleaching powder solution and hydrochloric acid, to convert all sulphur to sulphate, the mixture filtered, and the sulphate determined by addition of barium chloride to the filtrate. Care must be taken that the solution smells strongly of chlorine after the oxidation.

4. **Oxidisable Sulphur.**—This is arrived at by difference, by estimating the sulphur originally present as sulphate in the waste and deducting the value so obtained from the total sulphur obtained under test 3. Two g. of the waste is boiled with hydrochloric acid, filtered, the insoluble matter washed with dilute hydrochloric acid, the filtrate nearly neutralised by addition of pure sodium carbonate and precipitated by barium chloride.

B. *The Chance-Claus Sulphur Recovery Process.*[1]

1. **Sulphur present as Sulphide.**—The apparatus employed consists of a flask fitted with a tap-funnel and gas-exit tube, the latter being connected with an absorption vessel, such as that shown in Fig. 193 (p. 408), charged with a solution of alkali hydroxide and preferably connected with an aspirator. Two g. of the waste and a small quantity of water are introduced into the flask, and hydrochloric acid, diluted with an equal volume of water, gradually run in from the funnel until decomposition is complete. The solution is then boiled to drive off the whole of the gas, much water being carried forward and condensed in the absorption vessel during the operation. When about one-third of the water has been evaporated and the two-thirds remaining in the flask are boiling hot, the funnel tap is opened, the apparatus allowed to cool, and the contents of the absorption vessel transferred to a 500 c.c. flask and made up to this volume. An aliquot part of the solution is taken, diluted considerably with well-boiled water, neutralised with acetic acid, and titrated with $N/10$ iodine solution, each 1 c.c. of which = 0·0016 g. S. (*Cf.* also p. 531 for estimation of sulphide-sulphur.)

2. **Sulphur present as Sulphide in Carbonated mud.**—Six g. is

[1] *Cf.* Lunge, *Z. angew. Chem.*, 1890, 3, 573. For a description of the process, see Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 945.

taken for the analysis, which is otherwise carried out exactly as under test 1.

3. **Sulphide-sulphur and Carbonic acid in vat waste.**—This determination is but seldom made. The apparatus required consists of a small flask fitted with a tap-funnel and connected with a U-tube filled with anhydrous copper sulphate, to absorb any hydrochloric acid that passes over, and a sufficiently large number of calcium chloride tubes to dry the gas. Beyond the drying tubes two potash bulbs are provided and these are in turn connected with a weighed calcium chloride tube. Two g. of the waste together with some water is introduced into the flask and a current of nitrogen then passed through the apparatus. The waste is decomposed by hydrochloric acid, the solution boiled, and all sulphuretted hydrogen and carbon dioxide carried forward to the absorption tubes by the current of nitrogen, which is continued for a considerable time. The gain in weight of the potash bulbs and final calcium chloride tube gives the weight of CO_2 and H_2S contained in the waste. The H_2S is determined by treating the potassium hydroxide solution as described above under test 1, and the CO_2 obtained by taking the difference between the two determinations.

4. **Sulphur present as Sulphide in solutions of calcium sulphide or sodium sulphide.**—Ten c.c. is diluted to 250 c.c., an aliquot part of this diluted with a large volume of air-free water, acidified with acetic acid, and titrated as under 1. Should thiosulphate be present, it is estimated as under 5 and deducted from the total. Should polysulphide be present, only the sulphur liberated as sulphuretted hydrogen and not that precipitated by addition of acid is shown by this method.

Averitt[1] dilutes 5 to 20 g. of the sample to 200 c.c., runs 10 c.c. into a 200 c.c. conical flask containing 15 c.c. of water, and titrates rapidly with $N/10$ iodine, with constant shaking, till the polysulphide yellow almost disappears, then adds a small crystal of nitroprusside, and continues the titration till the disappearance of the purple colour. This gives the sulphide, and further titration till the liquid is tinted by iodine (or till added starch turns blue) gives the thiosulphate present.

5. **Soda, Lime, and Thiosulphate in sulphur liquors.**—The total alkalinity ($CaO+Na_2O$) is determined by titrating 5 c.c. of the liquor with hydrochloric acid, using methyl orange as indicator. A second portion of 50 c.c. is treated with carbon dioxide to drive off all the sulphuretted hydrogen (tested by lead paper), the solution boiled to decompose the calcium bicarbonate, diluted to 500 c.c., allowed to settle, and 50 c.c. of the clear solution titrated as above, the acid required

[1] *J. Ind. Eng. Chem.*, 1916, 8, 623; *Analyst*, 1916, 41, 288.

representing the Na_2O present. The CaO is obtained as the difference of the two titrations.

A further portion of the carbonated liquor is titrated for thiosulphate by *N*/10 iodine solution, 1 c.c. of which = 0·006412 g. S as $Na_2S_2O_3$.

The separation of the various sulphur compounds has been described above (p. 531 *et seq.*).

6. Lime-kiln gases.—The carbon dioxide is estimated in any form of gas burette or in an Orsat apparatus (Fig. 149, p. 272); the latter allows the oxygen to be determined at the same time.[1]

7. Gas from the Gas-holder.—(*a*) The sulphuretted hydrogen and carbon dioxide together are estimated as in test 3.

(*b*) The sulphuretted hydrogen is determined in a wide-necked flask of known capacity, say about 500 c.c. The flask is fitted with a double bored rubber stopper through which pass two glass tubes, the one reaching nearly to the bottom of the flask, and the second ending just below the stopper. Both tubes are provided with taps outside the flask. The gas to be examined is passed through the flask until all air has been expelled; 20 or 25 c.c. of normal sodium hydroxide solution is then admitted through one of the taps, and after thorough shaking the liquor is poured off, the flask well washed out, and the liquor and washings made up to a known volume. An aliquot part of the solution is then diluted with a large volume of air-free water, acidified with acetic acid and titrated with iodine. It is advisable to use an iodine solution containing 11·463 g. I per litre, since 1 c.c. of such a solution corresponds to 1 c.c. H_2S measured at 0° and 760 mm. pressure; 1 c.c. of *N*/10 iodine corresponds to 1·108 (or with sufficient approach to accuracy 1·1) c.c. of H_2S at 0° and 760 mm.

Lunge and Rittener's method (*cf.* p. 615) can also be applied to the analysis of mixtures of carbon dioxide and sulphuretted hydrogen. The two gases are absorbed together by sodium hydroxide, and an aliquot part of the solution then transferred to a second burette and run into a measured volume of *N*/10 iodine solution, the excess of which is titrated back after the reaction.

8. Exit Gases from the Claus kiln.—These gases contain small amounts of sulphuretted hydrogen and sulphur dioxide, both of which compounds by interaction with iodine solution give rise to two molecules of hydriodic acid for each atom of sulphur present; but whilst the sulphuretted hydrogen does not cause any further increase in the acidity, the sulphur dioxide gives rise to an equivalent of sulphuric acid. The sum of $H_2S + SO_2$ is consequently measured by determining the quantity of iodine converted into hydriodic acid, and the sulphur dioxide by the determination of the acidity remaining after the hydriodic acid thus formed has been neutralised. Since, however, the passage of a

[1] See Block, *Z. Ver. deut. Zuckerind.*, 1920, p. 223.

large volume of gas through iodine solution volatilises a portion of the iodine, it is necessary to insert a vessel containing sodium hydroxide or, preferably, sodium thiosulphate solution. One or more litres of the gas are aspirated through 50 c.c. of $N/10$ iodine solution contained in a bulb-tube (Fig. 193, p. 408), followed by a similar tube filled with 50 c.c. of $N/10$ sodium thiosulphate solution. When the operation is finished, the contents of the two tubes are emptied into a beaker and titrated with $N/10$ iodine solution and starch; the number of c.c. required ($=n$) multiplied by 0·001603 gives the total sulphur present as SO_2+H_2S. The blue coloration is then removed by addition of a drop of thiosulphate solution, methyl orange added, and the solution titrated with $N/10$ sodium hydroxide. If the number of c.c. necessary to neutralise the solution be called m, then $m \times ·001603$ gives the quantity of sulphur present as SO_2, and $(n-m) \times ·001603$ that present as H_2S.

II. THE AMMONIA-SODA PROCESS

RAW MATERIALS

1. **Rock-salt and Brine** (*cf.* p. 501 *et seq.*).

2. **Gas liquor, Ammonium sulphate, and other Ammonium salts** are treated of in Vol. III., under the section "Ammonia," and are examined as there described.

3. **Limestone** (*cf.* p. 581).

4. **Quick Lime** is analysed as described under Bleaching powder, p. 582.

5. **Coal** }
6. **Coke** } (*cf.* p. 327 *et seq.*).

CONTROL OF WORKING CONDITIONS

1. **Ammoniacal Brine.**

(*a*) *Sodium chloride.* The solution is acidified by nitric acid, and the sodium chloride estimated by Volhard's method (p. 74), or by titration in the neutral or faintly alkaline solution as described on pp. 73 and 504.

(*b*) *Free and combined Ammonia.* Ten c.c. of the solution is diluted to about 100 c.c. with water and boiled in a distilling flask until all free ammonia and ammonium carbonate have been distilled into a measured volume of normal hydrochloric acid, the excess of which is determined by titration. When this has been done sodium hydroxide solution is added to the residue in the distilling flask and the distillation continued until all the combined ammonia has been liberated and absorbed in a further quantity of normal acid.

2. Bicarbonate vessels (Carbonators). — Free and combined ammonia are determined as under 1.

3. Mother liquors.

(*a*) *Free and combined Ammonia*, as above.

(*b*) *Unchanged Sodium chloride.* Ten c.c. is evaporated in a platinum dish, the residue ignited to drive off all ammonium chloride, and weighed.

4. Bicarbonate.

(*a*) *Total Alkalinity* (*cf.* p. 570 *et seq.*).

(*b*) *Carbon dioxide* (*cf.* p. 570 *et seq.*).

(*c*) *Moisture*, determined by ignition, the carbonic acid found under (*b*) and the corresponding water from bicarbonate being deducted.

5. Ammonia distillation.

(*a*) *Free and combined Ammonia*, in the mother liquor, as above, under 1 (*b*).

(*b*) *Milk of Lime*, as under Bleaching powder, p. 583.

(*c*) *Excess of Lime in the stills.* One hundred c.c. is boiled until all the ammonia has been driven off, ammonium sulphate is then added and the boiling continued. The ammonia so liberated corresponds to the excess of lime present; it is absorbed in normal acid, and titrated.

6. Lime-kiln gas.—Determination of carbon dioxide (*cf.* p. 540).

7. Analysis of the Finished Product, as described under "Finished Soda Products," p. 548.

III. MANUFACTURE OF CAUSTIC SODA

The methods described are restricted to those relating to the manufacture of caustic soda by the lime process; the methods involved in the Löwig process (causticising by ferric oxide), follow naturally from the former. The analysis of the liquors obtained in the electrolytic processes is referred to on p. 544.

A. Causticised Liquor

This liquor is examined in the same way as the vat liquors of the Leblanc process (p. 527 *et seq.*); as a rule, only the specific gravity, total alkalinity, sodium carbonate, and sulphur compounds are estimated. A table showing the percentage of sodium hydroxide corresponding to various specific gravities is given under Caustic Soda, p. 565.

B. Fished Salts

The fished salts from the strong liquors consist essentially of monohydrated sodium carbonate and anhydrous sulphate; those fished from weaker liquors contain the same two salts in the hydrated condition.

For analysis, 50 g. of the salts are dissolved in water and made up to 1000 c.c.

1. **Total Alkalinity** is determined in 20 c.c. of the solution, exactly as in the case of caustic soda (p. 566).

2. **Sodium chloride.**—Twenty c.c. is treated with nitric acid in excess, boiled to decompose sulphur compounds, and filtered if necessary; after neutralising the excess of nitric acid with sodium carbonate, the solution is titrated with silver nitrate solution as described on pp. 73 and 504.

3. **Sodium sulphate.**—Twenty c.c. is acidified with hydrochloric acid, and hot barium chloride solution added to the boiling solution.

4. **Sodium sulphate from oxidisable sulphur compounds** (sodium sulphite and thiosulphate).—Twenty c.c. of the solution is treated with bleaching powder solution in excess, followed by hydrochloric acid, until the solution acquires an acid reaction and smells distinctly of chlorine (*cf.* p. 528). Barium chloride is then added and the precipitated barium sulphate collected and weighed. From the weight so obtained the weight of barium sulphate obtained in test 3 must be deducted.

C. CAUSTIC "BOTTOMS"

Caustic bottoms are examined for insoluble matter, total alkalinity, and sodium carbonate.

1. **Insoluble matter.**—Twenty g. of the sample is dissolved in water, and the solution filtered into a 500 c.c. flask. The insoluble matter is well washed, burnt whilst still moist in a platinum crucible, ignited, and weighed.

2. **Total Alkalinity.**—The filtered solution is made up to the 500 c.c. mark, and 50 c.c. is titrated hot with normal hydrochloric acid, using phenolphthalein as indicator. Methyl orange is not suitable owing to the presence of alumina, the quantity of which may amount to 2 or 3 per cent.[1]

3. **Sodium carbonate** is determined as described under Caustic Soda (p. 567).

D. LIME MUD

The lime mud is examined for sodium hydroxide and sodium carbonate, free lime, and calcium carbonate.

1. **Total Soda.**—Ammonium carbonate is added to the mud and the mixture evaporated to dryness to decompose all insoluble sodium compounds. The operation is repeated, the whole of the ammonium carbonate driven off, the residue washed with hot water, filtered, and the filtrate titrated for alkalinity. The result is best expressed in terms of Na_2O (0·031 g. per 1 c.c. normal acid), although the sodium found

[1] Lunge, *Z. angew. Chem.*, 1890, 3, 300.

may originally have been present partly as hydroxide and partly as carbonate.

2. **Caustic Lime.**—The mud is titrated with normal hydrochloric acid, employing phenolphthalein as indicator, as described on p. 525. From the result obtained, the value found under test 1, so far as this represents sodium hydroxide, must be deducted; no appreciable error will be introduced if the amount to be deducted is assumed as equal to half the value found under 1.

3. **Calcium carbonate.**—The total calcium is determined by titrating with acid and methyl orange and the caustic lime found under test 2 deducted from the total.

IV. ELECTROLYTIC ALKALI LIQUORS

The methods of analysis are the same, so far as the works tests are concerned, for both potash and soda solutions. In the case of potassium compounds a determination of the potassium in the finished product should, of course, be made; for this purpose the methods described in the section "Potassium Salts," Vol. II., are applicable. For the sake of brevity the expressions sodium carbonate, caustic soda, sodium chloride, etc., are to be taken to include the corresponding potassium compounds, when potassium compounds are the raw materials.

The essential products found in the liquors produced in the electrolysis of sodium chloride are:—sodium hydroxide, sodium carbonate, sodium chloride, sodium hypochlorite, and sodium chlorate.

These are the same as those found in "Eau de Javel," the commercial bleaching solution in which sodium is the base, though the proportions are very different in the two cases. The same methods of analysis are, however, applicable in both instances; these are given in the section dealing with Bleaching compounds (p. 610).

V. CRUDE FUSED SODA OF THE CELLULOSE INDUSTRY

By this name[1] is understood the product which results when the waste alkaline liquors obtained in the manufacture of cellulose from wood or straw by the "sulphite process" are, after addition of sodium sulphate, evaporated to dryness and calcined. The product consists essentially of carbonate, hydroxide, silicate, sulphide, sulphite and sulphate of sodium, but contains, in addition to these, small amounts of

[1] Cf. *Z. angew. Chem.*, 1901, **14**, 1102; *J. Soc. Chem. Ind.*, 1901, **20**, 1231.

sodium chloride, iron oxide, lime, magnesia, and alumina. Since these latter substances are without influence on the process, the amount present is seldom determined. A correct knowledge of the composition of the crude fused soda (recovered soda) is essential to the proper carrying out of the boiling operation, and indicates which constituents are to be removed and which to be added for successful working. Although the substances actually present in this product are the same as those in Leblanc black ash, the proportions differ considerably, for crude fused soda contains very large quantities of sulphide and also marked quantities of silicate, especially when straw has been treated.

The methods employed for the determination of the extremely small percentages of sulphide and silicate present in Leblanc liquors, although sufficiently exact for such purposes, are not directly applicable to the analysis of the wood-pulp product, and, as Lunge and Lohöfer[1] have shown, may easily lead to wholly unreliable results. A consideration of special importance is the fact that the separation of carbonate and hydroxide by means of barium chloride is quite impossible in the presence of silicate; thus from a solution of sodium metasilicate only a portion of the silica (50-60 per cent.) is precipitated, even in the presence of a very large excess of the reagent. As the result of their investigations, Lunge and Lohöfer recommend the following method for determining the chief constituents of crude fused sodium carbonate.

Fifty g. of the average sample is dissolved by continued shaking with 500 c.c. of water free from air and carbon dioxide. Solution is effected in a litre flask at a temperature of 45°, and the solution is cooled and diluted to 1000 c.c. before taking portions for analysis.

1. **Insoluble matter** is determined in the usual manner, by treating a portion of the sample with water, filtering, washing, and drying the residue.

2. **Alkalinity.**—Twenty c.c. (= 1 g. substance) is titrated with normal hydrochloric acid and phenolphthalein till the solution becomes colourless, when methyl orange is added and the titration continued until the change to red takes place. The number of c.c. required for each of these stages is noted. The titration must be carried out in the cold solution, and the best results are obtained if the temperature is not much higher than 0° C. (*cf.* p. 530). The solution, which is originally colourless, assumes a very faint yellow tinge when the colour change with phenolphthalein is reached; on further addition of acid the solution becomes strongly yellow and milky sulphur is deposited; but the colour change with methyl orange is quite distinct.

3. **Sulphide and Sulphite.**—Twenty c.c. (= 1 g. substance) is diluted to about 200 c.c. with air-free water, acidified with acetic acid and rapidly titrated with *N*/10 iodine solution, using starch paste as

[1] *Z. angew. Chem.*, 1901, **14**, 1125; *J. Soc. Chem. Ind.*, 1902, **21**, 70.

indicator. The sulphide present is found by deducting from the value so obtained the equivalent of the sulphite found under 4.

As there is a risk of loss of sulphuretted hydrogen when the titration is carried out in an acidified solution, Conroy[1] recommends adding the sulphide liquor either to a measured volume of an acidified $N/10$ iodine solution until the latter is decolorised, or adding a definite volume to an excess of iodine solution and titrating back with sodium thiosulphate.

4. **Sulphite.**—The sulphide present is precipitated by adding a solution of sodium zincate (prepared by adding sodium hydroxide solution to a solution of zinc acetate until the precipitate first formed redissolves) to 100 c.c. of the solution, the whole made up to 250 c.c. and filtered through a dry filter paper. Fifty c.c. of the filtrate (= 1 g. substance) is acidified with acetic acid and titrated as above with $N/10$ iodine solution and starch, the iodine required corresponding to the sulphite present.

5. **Silicate.**—Twenty c.c. of the solution is treated with excess of hydrochloric acid, evaporated to dryness, and the silica estimated gravimetrically in the usual way. One part $SiO_2 = 2{\cdot}032$ parts Na_2SiO_3. It is best to add the hydrochloric acid in an atmosphere of carbon dioxide, excluding air as far as possible, thus preventing oxidation of the sulphuretted hydrogen and sulphur dioxide, so that the filtrate from the silica may be available for the determination of sulphate.

6. **Sulphate** is determined as barium sulphate by the addition of barium chloride to the acidified filtrate from the silica determination. This method is only exact provided all oxidation has been excluded during the addition of the hydrochloric acid in 5. Further, incorrect results are obtained when relatively large quantities of thiosulphate[2] are present, but this point has little bearing on the analysis of wood-pulp soda, as thiosulphate is not likely to be present in the fresh material.

The calculation of the quantities of the various constituents present is most easily carried out by comparing the equivalents of the normal solutions employed, as will be evident from the following example of an actual analysis:—

1. Insoluble matter.

(*a*) 10.0039 g. substance gave 1.0836 g. residue.
(*b*) 10.0000 g. „ 1.0805 g. „
Weight of Ignited Residue.
(*a*) 1.0000 g., thus giving 0.0836 g. carbonaceous matter.
(*b*) 0.9904 g., „ 0.0901 g. „

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[1] Private communication.

[2] *Cf.* Richardson and Aykroyd, *J. Soc. Chem. Ind.*, 1896, **15**, 171; *Annual Report on Alkali, etc., Works*, 1899, p. 47; also, Dobbin, *J. Soc. Chem. Ind.*, 1891, **10**, 218.

2. Alkalinity in c.c. $N/5$ HCl.

With phenolphthalein, 49.39; 49.33; mean, 49.36 c.c.

" methyl orange, 76.74; 76.74; mean, 76.74 c.c.

3. $Na_2S + Na_2SO_3$.

$\left.\begin{array}{l}\text{40.23 c.c. } N/10\text{ I}\\ \text{40.27 c.c. } N/10\text{ I}\end{array}\right\}$ Mean, 40.25 c.c. $N/10$ I.

4. Na_2SO_3.

$\left.\begin{array}{l}\text{0.40 c.c. } N/10\text{ I}\\ \text{0.40 c.c. } N/10\text{ I}\end{array}\right\}$ Mean, 0.40 c.c. $N/10$ I.

5. Na_2SiO_3.

$\left.\begin{array}{l}\text{0.0699 g. } SiO_2\\ \text{0.0701 g. } SiO_2\end{array}\right\}$ Mean, 0.0700 g. SiO_2.

6. Na_2SO_4.

$\left.\begin{array}{l}\text{0.0536 g. } BaSO_4\\ \text{0.0534 g. } BaSO_4\end{array}\right\}$ Mean, 0.0535 g. $BaSO_4$.

Calculation.

1 c.c. $N/5$ HCl	corresponds to	0.0106 g. Na_2CO_3	and to	0.0080 g. NaOH.
1 c.c. $N/10$ I	"	0.0039 g. Na_2S	"	0.0063 g. Na_2SO_3.
1 g. SiO_2	"	2.028 g. Na_2SiO_3.		
1 g. Na_2SiO_3	"	81.63 c.c. $N/5$ HCl.		
1 g. $BaSO_4$	"	0.6089 g. Na_2SO_4.		

The 76.74 c.c. $N/5$ HCl with methyl orange correspond to the :—

$Na_2CO_3 + NaOH + Na_2SiO_3 + Na_2S + 1/2\ Na_2SO_3$ present.

The 49.36 c.c. $N/5$ HCl with phenolphthalein correspond to the :—

$NaOH + Na_2SiO_3 + 1/2\ Na_2S + 1/2\ Na_2CO_3$ present.

$$[76.74 - 0.10\ (\text{for } 1/2\ Na_2SO_3)] - 49.36 = 27.28 \text{ c.c. } N/5 \text{ HCl}.$$

$$2 \times 27.28 = 54.56 \text{ c.c. } N/5 \text{ HCl} = Na_2S + Na_2CO_3.$$

$$40.25 \text{ c.c. } N/10 \text{ I} = Na_2S + Na_2SO_3.$$

$$40.25 - 0.40 = 39.85 \text{ c.c. } N/10 \text{ I} = Na_2S.$$

$$0.40 \text{ c.c. } N/10 \text{ I} = Na_2SO_3.$$

$$54.56 - \frac{39.85}{2} = 34.64 \text{ c.c. } N/5 \text{ HCl} = Na_2CO_3.$$

$$49.36 - 27.28 = 22.08 \text{ c.c. } N/5 \text{ HCl} = NaOH + Na_2SiO_3.$$

1 g. substance, therefore, contains :—

Na_2CO_3	=	34.64×0.0106	=	0.3672 g.
Na_2SiO_3	=	0.0700×2.028	=	0.1420 g.
	(=	11.59 c.c. $N/5$ HCl)		
NaOH	=	$(22.08 - 11.59) \times 0.008$	=	0.0839 g.
Na_2S	=	39.95×0.0039	=	0.1554 g.
Na_2SO_3	=	0.40×0.0063	=	0.0025 g.
Na_2SO_4	=	0.0535×0.6089	=	0.0326 g.
Insoluble matter	=	Residue ÷ 10	=	0.1081 g.
		(of which the carbonaceous matter	=	0.0086 g.)

VI. FINISHED PRODUCTS OF THE SODA INDUSTRY

The various products of the manufacture are: soda ash, soda crystals, crystal carbonate, caustic soda, sesquicarbonate and bicarbonate, together with an intermediate product known as caustic ash; the method of analysis of the last does not call for special comment.

The individual products vary somewhat in their properties according to the method of manufacture. Thus, for example, a non-carbonated ash made by the Leblanc process may contain both caustic soda and sodium sulphide, whilst the presence of these compounds is practically impossible in the product of the ammonia-soda process. The chief impurity of Leblanc soda, according to percentage, is sodium sulphate, whilst in ammonia-soda the chief impurity is chloride. Commercial bicarbonate prepared by the ammonia-soda process may contain a small percentage of ammonia, whilst in bicarbonate prepared from soda crystals, ammonia is never present. Generally speaking, however, the same methods are adopted for the examination of any individual product, irrespective of its origin. Any special characteristics of importance dependent on the process of manufacture will be referred to in the description of the methods of analysis employed.

Special attention should be paid to the methods of sampling given on p. 8.

A. Soda Ash

This product consists essentially of sodium carbonate, but it may contain as impurity, small quantities of other sodium salts together with alumina, ferric oxide, water, etc.

Chemically pure sodium carbonate[1] contains 58·49 per cent. Na_2O, and 41·51 per cent. CO_2, and has a specific gravity of 2·5. Various values have been found for the melting-point by different observers; Carnelly gives 814°, le Chatelier 810°, Victor Meyer 849°. On fusion, a small quantity of sodium oxide is formed, and at a yellow heat the loss of carbon dioxide may rise to 1½ per cent. This loss on heating is inconsiderable at temperatures below the melting-point and may be altogether obviated by heating in a current of carbon dioxide. No loss occurs below a temperature of 300° (*cf.* p. 49).

The first of the following tables gives the percentage content corresponding to the various specific gravities of solutions of pure sodium carbonate, together with the corresponding percentage of decahydrated

[1] For further details, *cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 43.

1. Specific Gravity of Solutions of Sodium Carbonate at 15° C. = 60° F.

Specific Gravity.	Percentage by Weight.		Kilos per 1 cubic metre.	
	Na_2CO_3.	$Na_2CO_3\ 10H_2O$.	Na_2CO_3.	$Na_2CO_3\ 10H_2O$.
1·007	0·67	1·807	6·8	18·2
1·014	1·33	3·587	13·5	36·4
1·022	2·09	5·637	21·4	57·6
1·029	2·76	7·444	28·4	76·6
1·036	3·43	9·251	35·5	95·8
1·045	4·29	11·570	44·8	120·9
1·052	4·94	13·323	52·0	140·2
1·060	5·71	15·400	60·5	163·2
1·067	6·37	17·180	68·0	183·3
1·075	7·12	19·203	76·5	206·4
1·083	7·88	21·252	85·3	230·2
1·091	8·62	23·248	94·0	253·6
1·100	9·43	25·432	103·7	279·8
1·108	10·19	27·482	112·9	304·5
1·116	10·95	29·532	122·2	329·6
1·125	11·81	31·851	132·9	358·3
1·134	12·61	34·009	143·0	385·7
1·142	13·16	35·493	150·3	405·3
1·152	14·24	38·405	164·1	442·4

2. Specific Gravity of Solutions of Sodium Carbonate in degrees Twaddell at 15° C. = 60° F.

Degrees Twaddell.	Percentage by Weight.		Lbs. per 1 cubic foot of solution.	
	Na_2O.	Na_2CO_3.	Na_2O.	Na_2CO_3.
1	0·28	0·47	0·172	0·294
2	0·56	0·95	0·350	0·598
3	0·84	1·42	0·525	0·898
4	1·11	1·90	0·707	1·209
5	1·39	2·38	0·889	1·521
6	1·67	2·85	1·070	1·830
7	1·95	3·33	1·257	2·149
8	2·22	3·80	1·441	2·464
9	2·50	4·28	1·631	2·788
10	2·78	4·76	1·852	3·116
11	3·06	5·23	2·012	3·440
12	3·34	5·71	2·206	3·772
13	3·61	6·17	2·396	4·097
14	3·88	6·64	2·591	4·430
15	4·16	7·10	2·783	4·759
16	4·42	7·57	2·981	5·098
17	4·70	8·04	3·181	5·439
18	4·97	8·51	3·382	5·783
19	5·24	8·97	3·582	6·125
20	5·52	9·43	3·783	6·468
21	5·79	9·90	3·989	6·821
22	6·06	10·37	4·197	7·177
23	6·33	10·83	4·403	7·529
24	6·61	11·30	4·615	7·891
25	6·88	11·76	4·825	8·249
26	7·15	12·23	5·040	8·617
27	7·42	12·70	5·256	8·988
28	7·70	13·16	5·465	9·354
29	7·97	13·63	5·691	9·713
30	8·24	14·09	5·908	10·103

sodium carbonate, and the weight of sodium carbonate, anhydrous and hydrated, contained in 1 cubic metre of solution at 15° C. The data (at 15°) are calculated by Lunge from Gerlach's determinations. The second table gives corresponding data for degrees Twaddell, the percentage content of Na_2O and of Na_2CO_3, and the content of these per cubic foot of solution. The third table (at 30°) is based on Lunge's own determinations, and deals with the stronger liquors which frequently occur in practice and which can only exist above the ordinary atmospheric temperature.

3. Specific Gravity of Concentrated Solutions of Sodium Carbonate at 30° C. = 86° F.

Specific Gravity.	Degrees Twaddell.	100 lbs. contain lbs.		1 litre contains grms.	
		Na_2CO_3.	Na_2CO_3 10 H_2O.	Na_2CO_3.	Na_2CO_3 10 H_2O.
1·310	62	28·13	75·91	368·5	994·5
1·300	60	27·30	73·67	354·9	957·4
1·290	58	26·46	71·40	341·3	921·0
1·280	56	25·62	69·11	327·9	884·7
1·270	54	24·78	66·86	314·7	849·2
1·260	52	23·93	64·59	301·5	813·2
1·250	50	23·08	62·15	288·5	778·5
1·240	48	22·21	59·94	275·4	743·0
1·230	46	21·33	57·55	262·3	707·8
1·220	44	20·47	55·29	249·7	673·8
1·210	42	19·61	52·91	237·3	640·3
1·200	40	18·76	50·62	225·1	607·4
1·190	38	17·90	48·31	214·0	577·5
1·180	36	17·04	45·97	201·1	542·6
1·170	34	16·18	43·38	189·3	510·9
1·160	32	15·32	41·34	177·7	479·5
1·150	30	14·47	39·04	164·4	449·0
1·140	28	13·62	36·75	155·3	419·0

According to Lunge,[1] these tables not only give the percentage of Na_2CO_3 in solutions of pure sodium carbonate, but they give with almost equal accuracy the percentage of solid matter, that is, sodium carbonate plus impurities, in ordinary vat liquor (*cf.* p. 527).

A table showing the influence of temperature from 0° to 100° on the specific gravity of sodium carbonate solutions has been published by Lunge.[2] Liebig[3] has made use of Lunge's figures in calculating the mean values given in the following table.

[1] *Chem. Ind.*, 1881, 4, 376.

[2] *Technical Chemist's Handbook*, 2nd edition, 1916, p. 176.

[3] Post, *Chem. tech. Analyse*, 2nd edition, vol. i., p. 795.

4. Influence of Temperature on the Specific Gravity of Sodium Carbonate Solutions.

(Approximate mean values for $\pm$ 1° C.)

For Temperatures from					For Specific Gravities		
0° to 30°.	30° to 40°.	40° to 50°.	50° to 70°.	70° to 100°.	From	To	
0·0002	0·0004	0·0004	0·0005	0·0005	1·010	1·050	at 15°
0·0003	0·0004	0·0004	0·0006	0·0005	1·060	1·070	
0·0004	0·0004	0·0004	0·0006	0·0006	1·080	1·110	
0·0004	0·0004	0·0005	0·0006	0·0006	1·120	1·170	
0·0004	0·0004	0·0006	0·0007	0·0007	1·180	1·200	
0·0005	0·0004	0·0005	0·0007	0·0007	1·210	1·240	
...	0·0005	0·0005	0·0007	0·0007	1·241	1·252	at 30°
...	0·0005	0·0005	0·0006	0·0008	1·263	1·285	

A very thorough investigation of the specific gravities of solutions of sodium carbonate and of sodium hydroxide has been published by R. Wegscheider and H. Walter;[1] the results differ but slightly from the figures given above up to the third decimal place.

The chemical analysis of commercial soda ash is generally confined to the determination of the available alkali or alkalimetrical degree; a complete analysis is, however, made from time to time as a check upon the process.

Determination of the available Alkali of Soda Ash.—The method generally used is as follows: 26·50 g. of soda ash is weighed off in a small beaker and dissolved by boiling with water in a larger vessel. The solution, together with the small amount of insoluble matter, is transferred to a 500 c.c. flask, made up to this volume after cooling to 15°, well shaken and filtered, if necessary, through a pleated filter paper covered by a watch-glass. Fifty c.c. of the filtrate is then titrated with normal hydrochloric acid and methyl orange. For an ash containing 98 per cent. Na_2CO_3, 49 c.c. of normal acid (1 c.c. = 2 per cent.) will be required for the titration.

In the method adopted by the German alkali manufacturers, the ash is always ignited before determining the percentage of alkali and the results calculated on the ignited material; this gives the only satisfactory results. 2·6525 g. is taken for the analysis, dissolved in water, and the solution titrated directly without filtering. Each 1 c.c. of normal acid corresponds to 2 per cent. Na_2CO_3.

If the readings are made to $\frac{1}{40}$ c.c. in a 50 c.c. burette graduated in $\frac{1}{10}$ c.c., as may very readily be done in the manner described on p. 35, the error in the reading will not exceed 0·05 per cent. Na_2CO_3.

A normal solution of hydrochloric acid is employed, containing 36·46 g. HCl per litre, standardised both by means of chemically

[1] *Monatsh.*, 1905, **26**, 685; 1906, **27**, 13.

pure sodium carbonate and by silver nitrate (*cf.* p. 50). Methyl orange is the most convenient indicator.

It will be noted that in the method generally adopted in Britain, the alkalinity is determined in the solution only, whilst in the German method the alkalinity due to calcium carbonate, magnesium carbonate, ferric oxide, etc., in the insoluble matter is included in the total. This does not, however, cause any appreciable difference, at all events in the case of ammonia-soda, in which the total insoluble matter (inclusive of sand, carbonaceous matter, and other substances not affecting the alkalinity) does not exceed ¼ per cent.

Various methods are in vogue of stating the results of the titration, *i.e.* the strength of the ash. In the scale proposed by Gay-Lussac, the strength is expressed in terms of available soda, under which all the substances present which react with normal acid, such as carbonate, hydroxide, silicate, and aluminate, are included. Chemically pure sodium carbonate contains 58·49 per cent. Na_2O, and would thus correspond to 58·49 degrees Gay-Lussac. These degrees are generally referred to as "English" or "Newcastle" degrees, which, however, give the commercial strength always higher than the real value, as the table is calculated on the assumption that the chemical equivalent of Na_2CO_3 is 54, instead of the true value, 53·00.

In Germany, the "degrees" indicate percentage of Na_2CO_3, which is rational as applied to sodium carbonate itself; but the scale is also applied to all other sodium compounds, such as caustic soda, which act upon the test acid, and the strength is accordingly quoted in terms of a substance which occurs only as an impurity in the caustic alkali. The scale is, however, in general use commercially.

In France and Belgium, soda compounds of all kinds (also potash, baryta, etc.) are quoted on a basis similar to Gay-Lussac degrees, that is, according to their titrimetric value, leaving out, however, all reference to the particular alkali, whether sodium hydroxide, sodium carbonate, or potassium carbonate. The scale employed is that of Descroizilles, and the degrees indicate the quantity of sulphuric acid monohydrate (H_2SO_4) neutralised by 100 parts of the alkali examined. Since 10 parts of chemically pure sodium carbonate are equivalent to 9·252 parts H_2SO_4, the standard acid is prepared in such a way that 92·52 half cubic centimetres (so-called "divisions") will exactly neutralise 5 g. of pure sodium carbonate; or, in other words, the standard acid contains exactly 100 g. H_2SO_4 to the litre. The "Descroizilles sulphuric acid" is prepared by adding about 3150 c.c. of concentrated sulphuric acid to 50 litres of water, and standardising, as described on p. 50.

The following table (p. 553) shows the relationship between the English, German, and French degrees, and is applicable to sodium hydroxide and all soda products.

English, German, and French Commercial Alkalimetric Degrees.

Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).	Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).	Real Soda, Na_2O (Gay-Lussac Degrees).	English or Newcastle Degrees.	German Degrees, Na_2CO_3.	French Degrees (Descroizilles).
0·5	0·51	0·85	0·79	26·5	26·85	45·31	41·91	52·5	53·19	89·76	83·04
1	1·01	1·81	1·58	27	27·35	46·17	42·70	53	53·70	90·61	83·83
1·5	1·52	2·56	2·37	27·5	27·86	47·02	43·50	53·5	54·20	91·47	84·62
2	2·03	3·42	3·16	28	28·36	47·88	44·29	54	54·71	92·32	85·41
2·5	2·54	4·27	3·96	28·5	28·87	48·73	45·08	54·5	55·22	93·18	86·20
3	3·04	5·13	4·75	29	29·38	49·59	45·87	55	55·72	94·03	86·99
3·5	3·55	5·98	5·54	29·5	29·89	50·44	46·66	55·5	56·23	94·89	87·78
4	4·05	6·84	6·33	30	30·39	51·29	47·45	56	56·74	95·74	88·57
4·5	4·56	7·69	7·12	30·5	30·90	52·14	48·24	56·5	57·24	96·60	89·36
5	5·06	8·55	7·91	31	31·41	53·00	49·03	57	57·75	97·45	90·15
5·5	5·57	9·40	8·70	31·5	31·91	53·85	49·82	57·5	58·26	98·31	90·95
6	6·08	10·26	9·49	32	32·42	54·71	50·61	58	58·76	99·16	91·74
6·5	6·59	11·11	10·28	32·5	32·92	55·56	51·41	58·5	59·27	100·02	92·52
7	7·09	11·97	11·07	33	33·43	56·42	52·20	59	59·77	100·87	93·31
7·5	7·60	12·82	11·87	33·5	33·94	57·27	52·99	59·5	60·28	101·73	94·10
8	8·10	13·68	12·66	34	34·14	58·13	53·78	60	60·79	102·58	94·89
8·5	8·61	14·53	13·45	34·5	34·95	58·98	54·57	60·5	61·30	103·44	95·68
9	9·12	15·39	14·24	35	35·46	59·84	55·36	61	61·80	104·30	96·47
9·5	9·63	16·24	15·03	35·5	35·96	60·69	56·15	61·5	62·31	105·15	97·26
10	10·13	17·10	15·82	36	36·47	61·55	56·94	62	62·82	106·01	98·05
10·5	10·64	17·95	16·61	36·5	36·98	62·40	57·73	62·5	63·32	106·86	98·85
11	11·14	18·81	17·40	37	37·48	63·26	58·52	63	63·83	107·72	99·64
11·5	11·65	19·66	18·19	37·5	37·98	64·11	59·32	63·5	64·33	108·57	100·43
12	12·17	20·52	18·98	38	38·50	64·97	60·11	64	64·84	109·43	101·22
12·5	12·68	21·37	19·78	38·5	39·00	65·82	60·90	64·5	65·35	110·28	102·01
13	13·17	22·23	20·57	39	39·51	66·68	61·68	65	65·85	111·14	102·83
13·5	13·68	23·08	21·36	39·5	40·02	67·53	62·47	65·5	66·36	111·99	103·59
14	14·18	23·94	22·15	40	40·52	68·39	63·26	66	66·87	112·85	104·38
14·5	14·69	24·79	22·94	40·5	41·03	69·24	64·05	66·5	67·37	113·70	105·17
15	15·19	25·65	23·73	41	41·54	70·10	64·84	67	67·88	114·56	105·96
15·5	15·70	26·50	24·52	41·5	42·04	70·95	65·63	67·5	68·39	115·41	106·76
16	16·21	27·36	25·31	42	42·55	71·81	66·42	68	68·89	116·27	107·55
16·5	16·73	28·21	26·10	42·5	43·06	72·66	67·22	68·5	69·40	117·12	108·34
17	17·22	29·07	26·89	43	43·57	73·52	68·01	69	69·91	117·98	109·13
17·5	17·73	29·92	27·69	43·5	44·07	74·37	68·80	69·5	70·41	118·83	109·92
18	18·23	30·78	28·48	44	44·58	75·23	69·59	70	70·92	119·69	110·71
18·5	18·74	31·63	29·27	44·5	45·08	76·08	70·38	70·5	71·43	120·53	111·50
19	19·25	32·49	30·06	45	45·59	76·94	71·17	71	71·93	121·39	112·29
19·5	19·76	33·34	30·84	45·5	46·10	77·80	71·96	71·5	72·44	122·24	113·08
20	20·26	34·20	31·63	46	46·60	78·66	72·75	72	72·95	123·10	113·87
20·5	20·77	35·05	32·42	46·5	47·11	79·51	73·54	72·5	73·45	123·95	114·67
21	21·27	35·91	33·21	47	47·62	80·37	74·33	73	73·96	124·81	115·46
21·5	21·78	36·76	34·00	47·5	48·12	81·22	75·13	73·5	74·47	125·66	116·25
22	22·29	37·62	34·79	48	48·63	82·07	75·92	74	74·97	126·52	117·04
22·5	22·80	38·47	35·59	48·5	49·14	82·93	76·71	74·5	75·48	127·37	117·83
23	23·30	39·33	36·38	49	49·64	83·78	77·50	75	75·99	128·23	118·62
23·5	23·81	40·18	37·17	49·5	50·15	84·64	78·29	75·5	76·49	129·08	119·41
24	24·31	41·04	37·96	50	50·66	85·48	79·08	76	77·00	129·94	120·20
24·5	24·82	41·89	38·75	50·5	51·16	86·34	79·87	76·5	77·51	130·79	120·99
25	25·32	42·75	39·54	51	51·67	87·19	80·66	77	78·01	131·65	121·78
25·5	25·83	43·60	40·33	51·5	52·18	88·05	81·45	77·5	78·52	132·50	122·58
26	26·34	44·46	41·12	52	52·68	88·90	82·24				

Böckmann has drawn attention to the importance of always stating the results of the determination of the available alkali of soda ash on the dry material, so as to avoid disputes that may arise from any absorption of moisture that may have taken place during storage. When exposed to the air, soda ash takes up moisture fairly rapidly, and may absorb up to 10 per cent., whilst the loss on ignition of a soda ash properly handled in drawing from the calcining furnace and in packing, is always less than 0·1 per cent. For this reason, it is certainly desirable that the results should be expressed on the dry substance as well as on the sample as received.

GENERAL EXAMINATION OF SODA ASH

Under this heading the following determinations are included, in addition to the alkalinity determination: specific gravity, clearness of the aqueous solution, degree of fineness, matter insoluble in water, oxide of iron, sodium chloride, and sodium sulphate.

1. **Specific gravity or Density** (Böckmann).—The term specific gravity, or more correctly density, when applied to soda ash, does not mean the actual specific gravity as determined in the pyknometer, where the intervening space between the various particles of the ash is filled with a liquid, such as benzene, in which it is insoluble. For, as the impurities are about as dense as the soda ash itself (in round numbers, Na_2CO_3, 2·5; Na_2SO_4, 2·6; NaCl, 2·1), the actual specific gravity is largely independent of quality and of method of manufacture.

It is, however, necessary for many purposes to be able to express in figures the "bulkiness" of the ash, a property which depends on the method of manufacture and grinding adopted. The expression refers only to the cubic weight, that is, the weight of soda ash which can be closely packed into a vessel of definite capacity.

Böckmann recommends for this determination a strong cylindrical glass vessel, prepared by cutting off the upper part of a specimen bottle and grinding the edges of the lower part until the capacity is as nearly as possible 100 c.c.[1] It is not essential that the capacity should be 100 c.c., but the employment of a vessel of this size saves calculation. The capacity of the vessel to within 0·1 c.c. and its weight to within 0·1 g. are determined once for all, and both values are etched on the glass.

The ground and dry ash to be examined is filled into the vessel in about six separate portions, the glass being tapped on the table after each addition in order to pack the soda as closely as possible, so that a finger-nail does not make an impression in the mass.

[1] Special bottles for "cubic weight" determination of this capacity are made by Desaga, Heidelberg.

Finally, the ash standing above the top of the vessel is removed by sliding a small glass plate over the rim, after which the vessel and soda are weighed on a balance turning to 0·1 g. The density obtained is calculated to the second decimal place.

If the ash is filled into the vessel without pressure and tapping, the results are quite different from those obtained by the above method, but they are concordant amongst themselves and are consequently equally applicable in practice. This alternative method is more suited as an empirical test to be used in the packing-room. The vessel may conveniently consist of a box made of well-seasoned wood and having the internal dimensions $40 \times 25 \times 20$ cm., corresponding to a capacity of 20 litres, or similar suitable dimensions to give a capacity of 1 cubic foot. The soda ash is filled in with a clean wooden spade, care being taken to disturb the box as little as possible in introducing the material. The excess of ash is carefully removed by drawing a straight piece of wood over the top of the box, which is then weighed. The weight of the ash $\times 50$ gives the weight of ash per cubic metre.

Another plan for determining the density is to use a metal cylinder about 8·5 cm. high and 3 cm. diameter, filed down so as to hold 62·5 c.c. of water. The weight in grams of ash that fills a vessel of this capacity is equivalent to pounds per cubic foot, as 1 g. per 62·5 c.c. = 1 lb. per cubic foot.

Soda ash may be divided into three grades, according to the density—"light" (density 0·8 to 1·0), "medium" (about 1·0 to 1·25), and "heavy" (about 1·25 to 1·50).

2. **The Clearness of the Aqueous solution** (Böckmann).—The examination of the solution for turbidity is made by dissolving 25 g. of the ash in 500 c.c. of warm water in a beaker, and comparing the solution, after cooling, with a standard solution prepared in a similar manner.

The solutions obtained from ammonia-ash are relatively very clear, on account of the great purity of the product; this point is of advantage in colour and similar works. Naturally a commercial product like soda ash always contains traces of impurities and a perfectly clear solution is not to be expected.

3. **The degree of Fineness** (Böckmann).—The degree of fineness attained in the grinding is only determined in the case of a very heavy ash containing a considerable proportion of coarser particles, and only then, as a rule, when there is reason to suppose that the grinding has been insufficient. For the determination, 1000-1500 g. of the soda is sifted through a sieve of 35 cm. diameter and 2 mm. mesh, and the coarser particles remaining on the sieve weighed. The amount of the residue should not exceed 5 per cent. of the sample taken.

4. **Insoluble matter** (Böckmann).—Fifty g. of the sample (or 100 g. in the case of a very pure sample) is weighed off in a large beaker on a balance turning to 0·1 g. and sufficient water added to dissolve the ash; the contents of the beaker are agitated gently and continuously to prevent the formation of lumps, which would retard solution. The whole is then allowed to settle for from $\frac{1}{4}$ to $\frac{1}{2}$ hour in a warm place. As a rule, the insoluble matter settles well, and when this is the case the greater bulk of the solution can be syphoned off or decanted; the remainder is then filtered through a tared filter paper and the insoluble residue well washed with hot water. The two filter papers and insoluble matter are dried at 100° and weighed.

To determine the iron present in the insoluble matter, the dried and weighed filter is moistened with water and the precipitate treated on the filter with warm hydrochloric acid. The acid filtrate is treated with ammonia, and the precipitated ferric hydroxide filtered off and dissolved in dilute sulphuric acid (1 : 4). The solution is reduced by zinc and then titrated with permanganate. The titration may be made in the hydrochloric acid solution after reducing, diluting largely with water, and adding manganese sulphate solution, but the end-reaction is less sharp in this case.

5. **Sodium chloride.**—Two g. of ammonia-ash, or 5 g. of Leblanc ash, is dissolved in water and either exactly neutralised with nitric acid and titrated with silver nitrate solution (p. 73) with potassium chromate as indicator; or the determination may be made in acid solution by Volhard's method (p. 74).

6. **Sodium sulphate.**—Five or ten g. of the sample is dissolved in hydrochloric acid and the sulphate precipitated by the addition of a hot solution of barium chloride to the boiling solution.

THE COMPLETE ANALYSIS OF SODA ASH

This includes, in addition to the determinations already described, the determination of the various constituents of the insoluble matter (sand, carbonaceous matter, alumina, calcium carbonate, magnesium carbonate, and ferric oxide), and of bicarbonate, hydroxide, sulphide, sulphite, silicate, and aluminate of sodium. The five last-named impurities are only found in Leblanc soda. Such gross impurities as sulphide of iron, ferrocyanides, etc., which were formerly met with in Leblanc ash, need hardly be looked for to-day. In addition, it is necessary to determine the moisture, should any opportunity for its absorption have occurred between the times of manufacture and analysis. This may be done by drying in a desiccator over concentrated sulphuric acid, or with greater certainty, by drying for half an hour at 300°, or by gentle ignition.

Before carrying out the various determinations, it is advisable to ascertain whether sodium hydroxide, sodium sulphide, and sodium sulphite are present or not. For this purpose, a portion of the solution is shaken with an excess of barium chloride in absence of air, and the filtrate tested for alkalinity by means of sensitive litmus paper. A second portion of the alkaline solution is tested for sulphide by means of sodium nitroprusside or lead acetate paper, and a third portion examined for sulphite by testing whether the solution after acidifying with acetic acid and adding starch paste will decolorise a dilute solution of iodine.

For the analysis, 100 g. of the ash is weighed into a large beaker, agitated with warm water until solution is complete, the solution allowed to settle for about half an hour in a warm place, filtered through a tared filter paper into a litre flask, the insoluble matter thoroughly washed and the filtrate and washings made up to 1000 c.c.

1. **Sodium chloride**.—Twenty c.c. (= 2 g. ash) in the case of ammonia-ash, or 50 c.c. (= 5 g. ash) in the case of Leblanc ash, is neutralised with dilute nitric acid or dilute sulphuric acid, and titrated with silver nitrate solution (p. 73).

2. **Sodium sulphate**.—Fifty c.c. (= 5 g. ash) in the case of Leblanc soda, or 100 c.c. (= 10 g. ash) in the case of ammonia-soda, is rendered slightly acid by addition of hydrochloric acid and the sulphate precipitated in the hot solution by addition of barium chloride.

3. **Sodium bicarbonate**.—This only occurs in ammonia-soda, and is present only in traces. It is determined as described on p. 569. At least 5 g. of the sample should be taken and dissolved without agitation in cold water.

4. **Sodium hydroxide**.—This only occurs in incompletely carbonated Leblanc soda or in caustic ash. One hundred c.c. of the solution (= 10 g. ash) is taken and analysed as described on p. 526.

5. **Sodium sulphide**.—This is estimated by Lestelle's method,[1] by titrating 50 c.c. of the solution (= 5 g. ash) with an ammoniacal solution of silver nitrate. This solution, prepared by dissolving 13·825 g. pure silver in pure nitric acid, adding 250 c.c. of ammonia solution, and diluting to 1000 c.c., corresponds per 1 c.c. to 0·005 g. Na_2S. The solution of ash is heated to boiling, ammonia added, and the silver solution run in drop by drop from a burette, graduated in $\frac{1}{10}$ c.c., until no further precipitation of the dark-coloured silver sulphide results. To get the end-point more accurately it is advisable to filter the solution towards the end of the titration, repeating the filtration as often as may be necessary. Working with the above quantity of solution, each 1 c.c. of silver nitrate solution used corresponds to 0·1 per cent. Na_2S.

6. **Sodium sulphite**.—Fifty c.c. of the solution (= 5 g. ash) is

[1] *Comptes rend.*, 1862, 55, 739.

acidified with acetic acid, and after the addition of starch solution, titrated with $N/10$ iodine solution till the blue colour appears. Each 1 c.c. $N/10$ iodine solution equals 0·006303 g., or 0·1261 per cent. Na_2SO_3. Or the iodine solution containing 3·252 g. iodine per litre, described under black ash (p. 527), may be employed, each c.c. of which corresponds to 0·001615 g. or 0·0323 per cent. Na_2SO_3. A deduction must, if necessary, be made for the percentage of sulphide found under test 5, in the ratio of 1·3 c.c. $N/10$ iodine solution, or 5 c.c. of the weaker solution, for each 1 c.c. of the silver solution used.

7. **Sodium silicate and Sodium aluminate**.—One hundred c.c. of the solution (= 10 g. ash), or better, 10 g. of the ash directly weighed off and dissolved in water in the dish (to avoid error caused by the alkaline solution attacking the glass vessels), is acidified in a porcelain dish of about 1 litre capacity by the gradual addition of hydrochloric acid. The solution is then evaporated to dryness on the water-bath and finally dried at a higher temperature. On extraction with water, the silica remains behind, and the alumina goes into solution; each constituent is then determined in the usual way.

The silicate present in soda ash is too small in amount to interfere with the separation of the carbonate and hydroxide.

8. **Insoluble matter** (Böckmann).—The filter paper through which the solution of the 100 g. of ash has been filtered is moistened with water and the ferric oxide, alumina, and calcium and magnesium carbonates dissolved by addition of hydrochloric acid. The residue on the filter is well washed with hot water and the filter paper again dried and weighed, against the same paper as tare as before. This gives the sand and carbonaceous matter. The quantity of sand present is estimated by burning the filter paper and insoluble residue in a platinum crucible and deducting from the weight so obtained the ash found on burning the filter paper employed as tare; the difference between the weighings gives the percentage of sand.

The filtrate containing the portion of the residue soluble in hydrochloric acid is then submitted to the so-called "complete" commercial analysis, which consists in determining the iron oxide volumetrically as described on p. 452, and taking the rest of the insoluble matter as calcium carbonate; that is, the content in alumina and magnesium carbonate is not taken separately into account, but is looked upon as part of the calcium carbonate. This is sufficiently accurate for technical purposes.

In the method of determining the available alkali by direct titration of the soda solution, without previous filtration (p. 551), the following substances, if present, are determined in the titration along with the sodium carbonate: calcium and magnesium carbonates, the sesquioxides in the portion insoluble in water, sodium hydroxide, sodium

bicarbonate, sodium sulphide, sodium sulphite, sodium silicate, and sodium aluminate. If the titration is made in the filtered solution, any alkalinity due to basic substances in the insoluble matter is excluded. In any case, however, the influence of these impurities, both soluble and insoluble, plays but a small part in the titration of an average ash whether manufactured by the ammonia or Leblanc process. For example, supposing an ash gives on titration a total alkalinity, including that of the insoluble matter, equivalent to 98·4 per cent. Na_2CO_3 and the insoluble matter equals 0·33 per cent., a deduction of 0·3 is made from the total and the percentage of sodium carbonate present put down at 98·1. A 98° soda ash must at least consume acid equivalent to 98 per cent. Na_2CO_3 when the filtered solution is titrated, and the acid used may unhesitatingly be calculated to Na_2CO_3 for commercial purposes, since the soluble impurities are only present in traces, and for all the important technical applications of soda ash, with the exception of the manufacture of soda crystals, the impurities will react in the same manner as their equivalent of sodium carbonate.

Should it be necessary, in an exceptional case, to ascertain the real quantity of Na_2CO_3 present as accurately as possible, the sodium carbonate equivalent to the impurities determined as above, is deducted from the total available alkali. The direct determination of sodium carbonate, that is, of the carbonic acid content, is best made by the gas-volumetric method of Lunge and Marchlewski (p. 615).

A good soda ash should not contain more than 0·4 per cent. of matter insoluble in water, nor more than about 0·1 per cent. insoluble in hydrochloric acid, whilst the ferric oxide should not exceed 0·02 per cent. The impurities present in ammonia-ash frequently fall considerably below these limits.

The amount of sulphate present in ammonia-ash will not exceed 0·1 per cent., unless it has been specially added, while in the best Leblanc soda ash it may reach from ½ to 1 per cent., and in ash of low strength may even exceed 8 per cent.

Sodium chloride is present to the extent of from ½ to 2½ per cent. in ammonia-ash according as it is 98° or 96°/98° ash. Good Leblanc ash contains only from ¼ to ½ per cent.

9. Physical and Qualitative Tests. — Various physical and qualitative tests may be advantageously applied to the lower grades of ash made by the Leblanc process.[1]

A good quality of second grade ash should be white in colour even when hot, not yellow or reddish, though it cannot be expected to be as white as "refined alkali." On the other hand, when oxide of iron is present to any considerable extent, a yellowish product is often found to be better carbonated than a pure white product.

[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. ii., p. 737.

Frequently the ash possesses a bluish tinge, which arises from sodium manganate or from ultramarine, either formed in the black ash or, occasionally, purposely added. A grey colour indicates poor carbonating and calcining; as a rule such ash will contain much caustic alkali, together with incompletely oxidised sulphur compounds. Good ash should only show a few dark or red specks after grinding. The proportion of sodium hydroxide should in no case exceed 2 per cent. except in "caustic ash"; if the ash be intended for the manufacture of soda crystals, a maximum of 1 per cent. Na_2O is frequently stipulated, but it is difficult to keep within the limit, especially when, as in the Tyne works, all the mother liquors are worked up and carbonated, not by gas, but by sawdust. It is, however, readily done when Mactear's mechanical carbonator is employed. The ash should contain at most only very slight traces of sulphide. Even in the case of a moderately calcined and carbonated ash it should be impossible to detect sulphide by means of lead paper, and one drop of $N/10$ iodine should be sufficient to produce a blue coloration when added to a solution containing starch and 1 g. of the soda ash. An alkaline solution containing lead (sodium plumbate) acts better than the ordinary lead paper. Ash manufactured by the Leblanc process always contains minute quantities of sulphur compounds of the lower degrees of oxidation, but these can only be detected when large quantities of the ash, *e.g.* 50 g., are worked upon. A second quality ash may be regarded as satisfactory in this respect when the oxidisable sulphur compounds present do not exceed 0·1 per cent. of sulphur; for most purposes twice or three times this amount does no harm.

Sodium thiosulphate cannot occur in calcined soda ash, since it would be decomposed in the early stages of calcination. Sodium sulphite, on the other hand, is nearly always present, though in very small amount, in the poorer qualities of ash. It may be detected by iodine solution or other reagents (*cf.* p. 430).

A good second grade ash should not contain more than from 1 to $1\frac{1}{4}$ per cent. of insoluble matter; $1\frac{1}{2}$ per cent. should be looked upon as a maximum. The insoluble matter consists chiefly of calcium carbonate accompanied by alumina and silica; ferric oxide is only present in traces, except in ash of reddish-yellow colour and very bad appearance.

The moisture in freshly made ash ranges from $\frac{1}{4}$ to $\frac{1}{2}$ per cent., and when the ash is well packed it should not rise much over 1 per cent. even after some time. When the moisture reaches 2 per cent. the ash becomes lumpy and discoloured; it may absorb up to 10 per cent. of moisture if exposed to a damp atmosphere.

The two neutral salts, sodium chloride and sodium sulphate, which are always present in soda ash, are practically without effect, prejudicial

or otherwise, in the quantities normally contained in ordinary ash; this is, of course, not true when they are purposely added to reduce the strength.

Examination of Chemically Pure Sodium Carbonate

According to Krauch,[1] the natrium carb. puriss. usually employed for analytical work contains minute traces of iron, sodium chloride, and sodium sulphate. On this account only the purest and completely anhydrous product, natrium carb. sicc. chem. pur. should be employed for standardising solutions and other similar work. Kissling[2] found Merck's natrium carbonic. sicc. pulv. chem. pur. (for analysis), prepared from natr. carbonic. chem. pur. cryst., to consist only of sodium oxide, carbon dioxide, and water; it lost 0·63 per cent. CO_2 and 14·76 per cent. (corresponding to 1 molecule) H_2O at 150°, and therefore contained a little bicarbonate. According to Krauch, ordinary chemically pure anhydrous carbonate contains from 2 to 3 per cent. of water.

The various impurities are tested for as follows.[3]

* *Silica.* From 5 to 10 g. is evaporated with an excess of dilute hydrochloric acid, the residue dried for some time at 100° and then dissolved in a little hydrochloric acid and about 150 c.c. of water; the resulting solution should be clear and free from any flocculent precipitate of silica.

* *Sulphuric acid.* Five g. is dissolved in 75 c.c. of water, the solution made slightly acid by addition of hydrochloric acid, heated to boiling, and barium chloride added; no separation of barium sulphate should be apparent after twelve hours' standing.

* *Sodium chloride.* The slightly acid solution of 2 g. in 20 c.c. of water and dilute nitric acid should remain unaltered on addition of silver nitrate.

* *Arsenic.* Five g. of granulated arsenic-free zinc is placed in a Marsh generating flask of 200 c.c. capacity, dilute hydrochloric acid added and the reagents tested in the usual way for freedom from arsenic. Fifteen g. of the sodium carbonate is then dissolved in a small volume of water, the solution rendered acid by addition of pure dilute hydrochloric acid, added to the generating flask, and a steady slow evolution of gas maintained for half an hour; no indication of arsenic should occur during this time.

Soluble organic Iron compounds. Twenty-five g. of the carbonate is dissolved in 100 c.c. of lukewarm water, the solution filtered through a pleated filter paper and the filtrate treated with half its

[1] *The Testing of Chemical Reagents for Purity*, p. 281.

[2] *Chem. Zeit.*, 1890, 14, 136.

[3] The tests marked * are taken from Krauch, *loc. cit.*

volume of sulphuretted hydrogen water. The solution should remain absolutely colourless and show no greenish or dark coloration after standing for an hour. A blank test should be previously made with the distilled water employed.

Krauch (*loc. cit.*) makes a general examination for heavy metals in a similar manner: 20 g. of the carbonate is dissolved in 60 c.c. of water, the solution made acid by hydrochloric acid, and sulphuretted hydrogen water added; no coloration or turbidity should result. The solution should remain equally clear and free from green coloration after addition of ammonia and ammonium sulphide.

* *Phosphoric acid.* Twenty g. of the carbonate is dissolved in 60 c.c. of water, and nitric acid added in considerable excess, followed by a solution of ammonium molybdate. No sign of a precipitate should appear after the solution has been allowed to stand for two hours at a moderate temperature.

Ammonium salts. According to Krauch (*loc. cit.*), several grams of the carbonate are heated in a test tube containing a piece of moistened turmeric paper in the upper part of the tube, which is loosely closed. One-fiftieth of a per cent. of ammonia may be detected in this manner, whilst not less than 1 per cent. of ammonium salts can be recognised by smell without the paper. Detection by smell may be made much sharper by dissolving 10 g. of the carbonate in 500 c.c. of water, distilling the solution in the apparatus described on p. 476, under Ulsch's method of nitrate estimation, and smelling the gases evolved at the exit-tube from time to time.

* *Sodium thiosulphate.* The aqueous solution is acidified with acetic acid (1 : 50), and tested with silver nitrate. If, at the end of several minutes, the solution only shows a white opalescence (chlorine), it may be taken that neither thiosulphate nor arsenic is present in appreciable quantity. A reddish or yellowish turbidity indicates arsenic, whilst a brown or black turbidity indicates thiosulphate (*cf.* p. 569).

* *Potassium.* The yellow flame coloration produced by the carbonate should not show any, or only a transitory red tinge when viewed through cobalt glass or an indigo prism. According to Krauch, even fractions of a per cent. of potassium salts are sufficient to produce a persistent red coloration in the flame.

* *Sodium hydroxide.* Traces of this impurity are best recognised qualitatively by Dobbin's reagent, ammoniacal potassium mercury iodide. Kissling[1] gives the following method for its preparation. A solution of 5 g. of potassium iodide is treated with a solution of mercuric chloride until the precipitate formed just ceases to redissolve. The solution is filtered, and 1 g. of ammonium chloride added to the filtrate,

[1] *Chem. Zeit. Rep.*, 1898, 14, 136.

which is then cautiously treated with dilute sodium hydroxide solution until a slight permanent precipitate is formed. The solution is finally filtered and the filtrate diluted to 1 litre.

To apply the test, a small quantity of the carbonate solution is placed on a watch-glass and the reagent added; the least trace of hydroxide gives a yellow coloration.

B. Soda Crystals

Ordinary soda crystals consist essentially of decahydrated sodium carbonate, $Na_2CO_3.10H_2O$, which, in the chemically pure state, contains 21·678 per cent. Na_2O, 15·384 per cent. CO_2 (together, therefore, 37·06 per cent. Na_2CO_3), and 62·94 per cent. H_2O. A description of the properties of this salt and of other hydrated compounds of sodium carbonate containing less than 10 molecules of water of crystallisation is given in Lunge's *Sulphuric Acid and Alkali*.[1] The most important of these other salts is known as "Crystal Carbonate," which contains 82·0 per cent. of Na_2CO_3, 17 per cent. of H_2O, and 1 per cent. of other salts (practically $Na_2CO_3.H_2O$), but the quantity made is small when compared with that of the ordinary decahydrated soda crystals.

Commercial soda crystals seldom contain the theoretical quantity of water. There is either a small excess, which should not exceed 1 per cent., due to the drying only being carried out at ordinary temperature, or there is too little water, owing to efflorescence, from prolonged exposure to the atmosphere. Effloresced soda crystals lose considerably in appearance and this sometimes gives rise to complaint, although the change is entirely in the buyer's favour.

The commercial product is never free from sodium chloride and sodium sulphate. The percentage of sodium chloride should not appreciably exceed 0·5 per cent., whilst the percentage of sodium sulphate, the presence of which is essential for the production of hard crystals,[2] is seldom less than 1 and may rise to 2. A higher percentage of sulphate is to be regarded as inadmissible, especially as it is frequently added as an adulterant. Commercial soda crystals should test at least 34 per cent. Na_2CO_3 by titration, allowing for all impurities; generally 35 per cent. will be found, and in effloresced samples the percentage will naturally be still higher.

The estimation of the available alkali and of the impurities is carried out exactly as described under soda ash.

Grosser impurities, such as insoluble matter, iron, etc., were fairly frequent in the yellow crystals common in the early days of manufacture

[1] Vol. ii., pp. 42-81.

[2] *Cf.* Lunge's *Sulphuric Acid and Alkali*, vol. ii., p. 755.

but they are seldom found in the fine, colourless, transparent crystals which are now supplied. A yellow coloration may be due in part to organic matter.

"Chemically pure crystallised sodium carbonate" (natrium carb. cryst. chem. pur.) is examined as described on p. 561.

C. Caustic Soda

Chemically pure sodium hydroxide can only be obtained by treating metallic sodium with water and is not prepared on the manufacturing scale. Its properties are described in Lunge's *Sulphuric Acid and Alkali*,[1] where Honigmann's table of the boiling points of solutions of sodium hydroxide is also given.

The specific gravity of aqueous solutions of sodium hydroxide has been determined by various observers. Tünnermann's determinations (1827) were made use of by Schiff (1858) for calculating a formula connecting density with concentration, and this formula was employed by Gerlach (1867) for the preparation of his table of specific gravities which was in general use until twenty years ago. This table was revised by Hager (1883), and an independent series of determinations was published subsequently by Pickering[2] (1894). Bousfield and Lowry[3] have recently shown that all these determinations are unreliable, owing to the difficulty of preparing solutions of known concentration; in every case the solutions appear to have been standardised by titration, a method which they have shown to be inaccurate to the extent of from 0·2 to 0·3 per cent. Hager's table is in their opinion less accurate than that of Gerlach; they regard Pickering's relative values for the specific gravity at different concentrations as substantially accurate, but the absolute values as unreliable, to the extent of 0·001 at 50 per cent. sodium hydroxide, and roughly to a proportionate extent at the lower concentrations.

Bousfield and Lowry[4] have accordingly made a fresh series of determinations of the specific gravity of sodium hydroxide solutions, which is given in the following table; the determinations were made at 18° C., but in the original paper are also calculated by means of a series of temperature coefficients to 15°. The solutions were prepared from weighed quantities of metallic sodium and the densities determined by means of the pyknometer; the values may be regarded as accurate to within 0·01 per cent. of sodium hydroxide, and involve a possible error of 0·0001 in the sp. gr. of a 50 per cent. solution.

[1] Vol. ii., p. 81.

[2] *Phil. Mag.*, 1894 [v.] **37**, 359; *J. Chem. Soc.*, 1895, **67**, 545.

[3] *Phil. Trans.*, 1905, **204**, 253.

[4] *Loc. cit.*

Specific Gravity of Solutions of Sodium Hydroxide at 18° C. = 64°.4 F.

NaOH. Per Cent.	Specific Gravity.	NaOH. Per Cent.	Specific Gravity.
0	0·99866	26	1·2860
1	1·01003	27	1·2968
2	1·02127	28	1·3076
3	1·03241	29	1·3184
4	1·04349	30	1·3290
5	1·05454	31	1·3396
6	1·06559	32	1·3502
7	1·07664	33	1·3605
8	1·08769	34	1·3708
9	1·09872	35	1·3811
10	1·10977	36	1·3913
11	1·12082	37	1·4014
12	1·13188	38	1·4115
13	1·14294	39	1·4215
14	1·15400	40	1·4314
15	1·16505	41	1·4411
16	1·17610	42	1·4508
17	1·18714	43	1·4604
18	1·19817	44	1·4699
19	1·20920	45	1·4791
20	1·22022	46	1·4890
21	1·23121	47	1·4985
22	1·24220	48	1·5080
23	1·25317	49	1·5174
24	1·26412	50	1·5268
25	1·27506		

A detailed table, giving the variation of specific gravity with changes of temperature from 0° to 100° at intervals of 10°, is also given by Bousfield and Lowry.[1] A similar table up to temperatures of 50°, but based on the earlier determinations of specific gravity, is given in the *Technical Chemist's Handbook* (p. 190).[2]

It is important to bear in mind that solutions of sodium hydroxide prepared from commercial products show greater variations in the degree of purity than solutions of sodium carbonate or of acids.

The ordinary rules for sampling, described under "General Methods of Technical Analysis" (p. 4), are not applicable to caustic soda, which comes on to the market in solid blocks packed in iron drums. The block filling the drum is not perfectly uniform throughout; the portions most nearly representing the average are those next to the bottom and sides of the drum, as these portions have solidified fairly rapidly on packing; the central portions which have solidified more slowly are less regular in their composition, as the impurities, more especially chloride and sulphate, have time to accumulate in the fluid core. In sampling, pieces should therefore be taken from as many different parts

[1] *Loc. cit.*, p. 564.
[2] *Cf.* also, Wegscheider and Walter, *Monatsh.*, 1905, **26**, 685; 1906, **27**, 13.

as possible. In the works the sampling is best done while the material is still liquid; the most satisfactory procedure is to draw three samples from each pot as it is emptied, viz., from the top, the middle, and the bottom respectively, and to pour these, one after the other, on to a plate and to take the middle portion of the whole for analysis. The three lots can be readily separated, as the surfaces of the layers of each sample solidify before the pouring of the next.

The samples readily take up moisture and carbon dioxide, on the surface, shown by the formation of a bright white crust even when preserved in well-stoppered bottles; this crust should be removed by scraping before the samples are weighed for analysis.

According to Böckmann, the sample should be roughly powdered as rapidly as possible, to prevent absorption of moisture; if single pieces be taken instead of the more homogeneous coarse powder, differences up to 1 per cent. may result with different portions of the same product. Such powdering is not, however, to be recommended, since some absorption of moisture and of carbon dioxide cannot be avoided and may give rise to errors appreciably exceeding 1 per cent.

The chemical analysis of caustic soda is generally confined to the determination of the total alkalinity and of the caustic soda, or more correctly the available soda inclusive of sodium silicate and sodium aluminate. Sodium chloride, sodium sulphate, and water may also be determined. Other impurities are only present in small amount and are consequently only determined in exceptional cases; the methods described under black ash and soda ash are then employed.

Analysis of Caustic Soda.—Fifty g. of the sample, freed from crust by scraping, as described above, is dissolved in water, the solution made up to 1000 c.c., and portions of this solution withdrawn for the following tests.

1. The *Total Alkalinity* is determined by titrating 50 c.c. of the solution (= 2·5 g. substance) with normal acid, using methyl orange as indicator. The result is variously calculated according to the scale employed (see p. 552). In England the results are either expressed in percentage of "real Na_2O" or in percentage of "commercial Na_2O," the latter figure being arrived at by multiplying the percentage of real Na_2O by 31·4 and dividing by 31. In Germany the alkalinity is expressed as a percentage of sodium carbonate, and in France in degrees Descroizilles.

2. The *Sodium Hydroxide* actually present may be determined in various ways. The only other alkaline substance to be taken into account is sodium carbonate; the quantities of aluminate and silicate are extremely minute, except in the case of caustic bottoms (p. 543).

The most exact method of determining the carbonate is to determine the carbon dioxide evolved on treatment with a strong acid. This may

be done either gravimetrically by the Fresenius-Classen method, or more rapidly and accurately by the method of Lunge and Marchlewski (p. 615).

The method depending upon titration with phenolphthalein and hydrochloric acid, after the addition of an excess of barium chloride (p. 526), is almost equally exact. This method gives the caustic soda directly.

In the United Alkali Co.'s laboratory at Newcastle 40 g. of the caustic soda is placed in a flask connected with a series of three absorbing bottles or tubes containing a mixture of about 40 c.c. of 10 per cent. barium chloride solution, and 40 c.c. of 10 per cent. sodium hydroxide solution filtered after mixture. Excess of dilute hydrochloric acid is gradually added through a tap-funnel, and then the liquid is boiled and a current of air, free from carbon dioxide, passed through till all carbon dioxide has been expelled. The liquid from the absorbing vessels is quickly rinsed into a 500 c.c. flask, made up to the mark, and well shaken. Two portions of 100 c.c. each are titrated with acid, one turbid, the other after filtration; the difference between the two represents the carbonate present in the sample.

For routine testing in the works the following method is to be recommended. It is not quite so accurate as the above, but it has the advantage of rapidity and serves as a check on the total alkalinity (test 1). Fifty c.c. of the solution, preferably cooled nearly to 0°, is titrated first with hydrochloric acid and phenolphthalein until the red coloration just disappears, which occurs when all the sodium hydroxide has been neutralised and the carbonate present has been converted to bicarbonate; methyl orange is then added to the solution and the titration continued until the yellow colour changes to pink. If n c.c. of acid are required for the first part of the titration, and m additional c.c. for the second, $2m$ corresponds to the Na_2CO_3 present and $n-m$ to the NaOH.

3. The determination of *Chloride*, *Sulphate*, and other impurities is carried out as described under Soda Ash, p. 557.

4. *Water*. Caustic soda may contain up to 30 per cent. of water when it reaches a broker or analyst. This is more especially the case when samples have been sent in badly sealed boxes, etc.

In such instances the water cannot be accurately determined by direct heating in a porcelain crucible owing to unavoidable mechanical loss through small particles being carried away by the escaping steam; on the other hand, if caustic soda be heated in a drying oven to 140° a gain in weight may very easily occur, due to absorption of carbon dioxide; such a gain almost invariably occurs when the water content is low.

The moisture determination is therefore best made as described

under Salt (p. 506). About 5 g. of the caustic soda is heated to 150° on the sand-bath for three or four hours in an Erlenmeyer flask of the prescribed dimensions. The funnel must be kept in position the whole time (in this the method differs from that employed in the case of salt), to prevent absorption of carbon dioxide. The flask and funnel are placed on a marble slab, after the heating is completed, allowed to cool in the air, and finally weighed.

Caustic Salts are analysed in the same way as caustic soda.

D. Sodium Bicarbonate

Sodium bicarbonate, $NaHCO_3$, contains 36·90 per cent. Na_2O, 52·38 per cent. CO_2, and 10·72 per cent. H_2O. In the pure condition, that is, when fully saturated with carbon dioxide, it reacts alkaline towards litmus, and, according to earlier accepted views, neutral to phenolphthalein. Küster[1] states that in dilute solution it reddens phenolphthalein in consequence of hydrolysis, and Siemens[2] has found that such reddening is produced by even the purest bicarbonate. The solubility and other properties are described in Lunge's *Sulphuric Acid and Alkali*.[3]

On exposure to the air the powder loses carbon dioxide, even at the ordinary temperature, and much more rapidly at somewhat higher temperatures. The aqueous solution, in a similar manner, rapidly parts with some of its carbon dioxide and then contains appreciable quantities of the normal carbonate.

Commercial bicarbonate is very seldom absolutely free from normal carbonate, but the quantity of this should only be very small. Bicarbonate should dissolve in water to a perfectly clear solution and chloride and sulphate should only be present in traces. Formerly bicarbonate was frequently found to contain sodium thiosulphate, due to its having been manufactured from Leblanc soda liquors by the Deacon-Hurter process. Bicarbonate manufactured by the ammonia-soda process may contain a little ammonia as carbonate or chloride, but at the present time the high percentage (2·6 per cent. ammonium carbonate) found by Lehmann[4] is not likely to occur; a much smaller percentage than this would make itself evident by the odour.

Bicarbonate of soda is very largely used in medicine and in bakeries, and it should therefore not contain metallic impurities in sufficient quantity to be detectable by sulphuretted hydrogen or by ammonium sulphide. The detection of small quantities of arsenic is carried out as described on p. 433.

Qualitative analysis of Sodium bicarbonate.—This is directed

[1] *Z. anorg. Chem.*, 1896, **13**, 127.
[2] *Fischer's Jahresber.*, 1897, 455. See also Tillmans and Heublein, *Z. angew. Chem.*, 1911, **24**. 874.
[3] Vol. ii., p. 53.
[4] *Chem. Ind.*, 1887, **10**, 88.

in the first place to the examination for chloride and sulphate, which impurities should only be present in very small quantity; this applies also to ammonia. Thiosulphate is detected, according to Mylius,[1] by adding dilute sulphuric acid and zinc, and examining for sulphuretted hydrogen by means of lead paper. According to Musset,[2] very small amounts of thiosulphate can be detected by the grey coloration due to mercuric sulphide, which is formed when 5 g. of the bicarbonate are ground with 0·1 g. of calomel and two drops of water.

Thiocyanates are detected, according to Utescher,[3] by agitating a large quantity of the bicarbonate with water and testing the solution with ferric chloride in hydrochloric acid solution.

Several methods for detecting the presence of the normal carbonate in bicarbonate are known. The methods depending upon the reddening of phenolphthalein are, according to Küster's observations (*cf.* p. 568), inaccurate. The method usually employed is the reaction with mercuric chloride. A solution of mercuric chloride in two parts of water is added to a solution of the bicarbonate in fifteen parts of water, when a white cloudiness, which gradually becomes brown after several minutes, is produced. This method is, however, by no means reliable, and the same may be said of all other qualitative tests for the normal carbonate. The presence of the normal carbonate can only be proved with certainty by a quantitative examination.

The detection of normal carbonate by means of magnesium sulphate is absolutely untrustworthy. It is better, according to Leys,[4] to employ a saturated solution of calcium sulphate which, in the presence of sodium carbonate, gives a precipitate of amorphous calcium carbonate, which is easily distinguishable from the crystalline calcium sulphate.

Kubli[5] recommends the use of quinine hydrochloride, which is not precipitated by bicarbonate containing less than 2 per cent. of normal carbonate.

Quantitative analysis of Sodium bicarbonate consists in determining the percentage of available alkali and of carbon dioxide. As a matter of fact, the latter determination alone is sufficient.

The indirect method of determining total carbon dioxide by driving it off and noting the loss of weight in one of the known forms of apparatus, is not sufficiently exact. Trustworthy results can only be obtained by determining the carbon dioxide directly, either gravimetrically by absorption with soda lime, etc., or gas-volumetrically by the method of Lunge and Marchlewski as modified by Lunge and Rittener (p. 615).

The method described on p. 530 may also be employed, but since

[1] *Fischer's Jahresber.*, 1886, 282.
[2] *Z. angew. Chem.*, 1890, 3, 311.
[3] *Apoth.-Zeit.*, 1888, 610.
[4] *Chem. Centr.*, 1898, I., 752.
[5] *Ibid.*, 1898, II., 416.

this necessitates bringing the bicarbonate into solution, care must be taken to avoid loss of carbon dioxide during this operation. The determination is carried out as follows:—

5·0 g. is weighed off in a small beaker and dissolved in about 100 c.c. of water which has been previously thoroughly boiled and again cooled to 15° to 20°. Solution is effected in a large beaker of 900 to 1000 c.c. capacity, agitation of the solution being avoided as far as possible; the operation may be assisted by cautiously breaking up any lumps of bicarbonate that remain on the bottom of the beaker with a glass rod, care being taken not to stir up the solution at all violently. Unless these precautions be observed, loss of carbon dioxide may easily occur and the results obtained will not be reliable. The water employed should not be below 15° nor above 20° in temperature; in the former case, solution is difficult, and in the latter, loss of carbon dioxide is likely to result.

Ten g. of pure sodium chloride is then added to the solution, which is cooled to nearly 0°, and titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator, the titration being carried to the point where the red colour just vanishes ($=a$ c.c. acid). The jet of the burette should dip into the solution. Methyl orange is next added, and the titration continued until the colour changes to yellow ($=b$ c.c. acid). $2a$ c.c. correspond to the alkali present as Na_2CO_3, and $b-a$ to that present as $NaHCO_3$ (*cf.* p. 530).

Sundström's method,[1] which consists in adding sodium hydroxide to the bicarbonate solution until the latter has been converted into carbonate, this point being determined by the brown coloration produced by spotting with silver nitrate, has been examined by Lunge[2] and found to be reliable. It is, however, less convenient than the method described above, and is in no way more accurate.

Estimation of the total Carbon dioxide. This is a more reliable check than the above on the composition of bicarbonate; the quantity should at least reach 50 per cent. (theoretically, 52·34 per cent.). The best plan is to determine the carbon dioxide present as bicarbonate directly. A simple, rapid and exact method for this determination has been described by Lunge,[3] which consists in heating the sample to a definite temperature and determining the carbon dioxide driven off; the method is only applicable to solid bicarbonate and not to solutions.

The apparatus shown in Fig. 206 is employed in carrying out the test. It is connected with a bulb-nitrometer (p. 81), or preferably, with a gas-volumeter (p. 83), or with any other suitable apparatus for measuring or weighing the carbon dioxide evolved.

A glass tube, 65 mm. long and 6 mm. internal diameter, is fused

[1] Private communication to Professor Lunge. [2] *Z. angew. Chem.*, 1897, II, 169.
[3] *Z. angew. Chem.*, 1897, II, 522.

at one end to a wider tube, provided with a tightly fitting ground-in stopper, *a*, and at the other end with a capillary tube, *d*, 60 mm. long. The stopper *a* is continued in the form of a glass rod, *b*, 30 mm. long, which, whilst not ground into the tube, fits it fairly tightly. This leaves a free space, *c*, 35 mm. long and 6 mm. diameter, which is separated from the capillary by means of a small plug of asbestos or glass-wool. This free space will hold about 0·850 g. of powdered bicarbonate, a quantity which, provided the quality be good, will give rather more than 110 c.c. of carbon dioxide, measured at 0° and 760 mm. This volume can be readily measured in the universal gas-volumeter, which is graduated from 1 to 30 c.c. and from 100 to 140 c.c., the intervening space being taken up by the bulb. Should the free space in the decomposition tube be too small or too large for the measuring apparatus employed, it may be altered by making the glass rod *b* shorter or longer, as may be necessary.

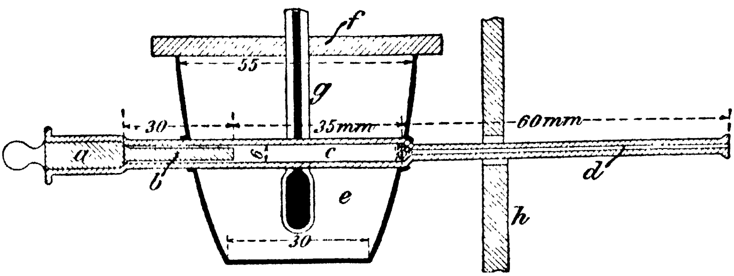

FIG. 206.

The stopper extension *b* allows the space *c* to be well heated without risk of cracking the ground-in portion *a*, and so permits this part to be made perfectly tight by using a little vaseline or other grease.

The heating is effected in the air-bath *e*, which consists of an iron crucible bored in two corresponding positions on opposite sides and covered with a piece of asbestos card, *f*, through which the thermometer *g* is placed. A sheet of asbestos card, *h*, is fixed over the capillary *d*; this card extends below the flame used to heat the crucible *e* and thus protects the gas-volumeter from the heat; an interval of at least ten minutes must be allowed after each operation before the volume of gas collected is adjusted and read off.

To carry out the determination, the tube is first weighed empty, then filled with bicarbonate and again weighed. Care must be taken that none of the bicarbonate remains in the portion fitted with the stopper *ab*; any particles adhering to the walls in this portion of the tube must be removed by a rubber-covered rod or other suitable contrivance before the stopper, which should be covered with a little vaseline, is inserted. The tube is then placed in the air-bath, as shown in Fig. 206,

so that the whole of the bicarbonate gets heated, and the free end of the capillary *d* connected with the side capillary tube of the gas-volumeter. The small capillary space between these two tubes is evacuated two or three times by lowering the levelling tube of the volumeter until a vacuum exists in the measuring tube, shutting off from the capillary and expelling the air from the measuring tube by raising the levelling tube. Three such evacuations may be carried out in the space of a minute. The levelling tube is then lowered and the air-bath heated by a flame of moderate size to between 260° and 270°, an operation requiring on the average about seven minutes. The heating is continued for a further three minutes, after which the tap connecting the capillary with the measuring tube is closed, the apparatus allowed to stand for about ten minutes to attain the atmospheric temperature and the levelling and reduction tubes adjusted in the usual manner to allow the volume of gas evolved to be read off directly as dry gas corrected to 0° and 760 mm. Since the gas is always collected moist in this determination the reduction tube must be set accordingly; the condensation of water is very small and exerts no influence on the reading. The percentage of carbon dioxide may be calculated directly from the volume read off, since the free capillary space is so small that no appreciable quantity of air remains after evacuating three times as described above. Lunge, however, recommends transferring the gas, after measurement, to an Orsat apparatus and proving that it is completely absorbable by alkali hydroxide, which he finds is always the case. One c.c. dry CO_2 at 0° and 760 mm. pressure weighs 1·9772 mg., and corresponds to 7·5493 mg. $NaHCO_3$. To arrive at the actual percentage of bicarbonate in the sample examined, the figure 7·5493 is multiplied by the number of c.c. of gas liberated and divided by the weight of substance taken. If it be desired to determine also the amount of normal carbonate present, a second portion of the sample may be titrated with normal acid and methyl orange, or the total carbon dioxide liberated by decomposing with hydrochloric acid may be determined (p. 615). In the latter case, twice the volume of carbon dioxide found in the bicarbonate estimation is deducted from the total carbon dioxide found, and the remainder calculated to normal carbonate.

The residue in the decomposition tube used in the determination of the bicarbonate can be washed out and titrated; this saves a weighing, but it is scarcely as accurate as the titration of a separate portion, owing to the risk of losing some of the material. This determination of normal carbonate is, as a rule, unnecessary.

Sodium Sesquicarbonat .— A certain quantity of naturally occurring soda is brought on to the market, chiefly from the Magadi deposits in British East Africa. It is intermediate in composition

between carbonate and bicarbonate, and approximates to the formula $Na_2CO_3 \cdot 2NaHCO_3 \cdot 3H_2O$. It is analysed by the same methods as are used for bicarbonate.

THE EXAMINATION OF COMMERCIAL LIQUID CARBON DIOXIDE

The following particulars are taken from a very complete investigation of the subject by Lange.[1] In determining the value of commercial liquefied carbonic acid, it is, as a rule, sufficient to find out what proportion of gases not absorbable by potassium hydroxide solution is contained in the liquid. It is usually unnecessary to determine the volume of air present in the gas space of the cylinder. This and the determination of the carbon dioxide present in the gas space need only be done in very exact work, when a series of samples otherwise similar have to be examined. In determining the percentage of air in samples of the gas drawn from the cylinder, it will usually suffice to determine the carbon dioxide in the gas space before and after the taking of the sample. The percentage of air present in the sample is then taken as the mean of the two determinations, provided that the carbon dioxide last examined is not perfectly air-free.

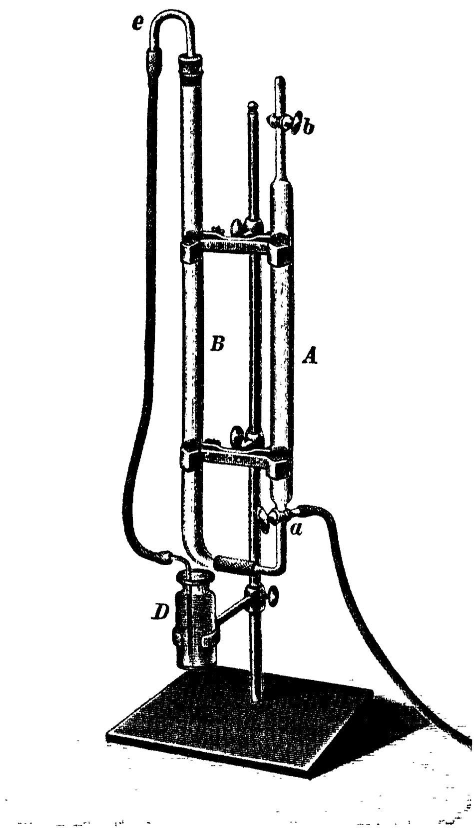

FIG. 207.

Any suitable form of apparatus for gas analysis may be employed for the determination of the contained air. Lange makes use of the modified Winkler gas-burette shown in Fig. 207.

The tube A has a capacity of 100 c.c. and is narrowed at the top to a tube of 5 c.c. capacity, graduated in $\frac{1}{20}$ c.c. It is connected at its lower end with the tube B by means of a piece of rubber tubing; a run-off tap is not provided. The bent tube *e* is connected by a length of rubber tubing with a glass tube, which dips into about 250 c.c.

[1] *Chem. Ind.*, 1900, **23**, 530; *J. Soc. Chem. Ind.*, 1901, **20**, 122.

of the solution contained in the bottle D, clamped to the stand. To charge the apparatus, potassium hydroxide solution of sp. gr. 1·297 is introduced into B in sufficient quantity to more than half fill the tubes B and A; the stopper carrying the bent tube *c* and the attached rubber tubing is then fixed in position in B, and the alkali solution driven out of the tube A, by blowing through a rubber tube attached above the tap *b*, till its level is at the tap *a*, which is then closed. There is now continuous liquid from *a* to the bottle D, which is now fixed at such a height on the stand that on opening *a* no alteration of level occurs. The liquid will now fall automatically to *a* whenever *b* is opened, so that successive analyses can be rapidly performed.

The examination of the carbon dioxide is carried out as follows. An adapting piece is screwed, using some luting material, into the outlet pipe of the cylinder, which is placed in a vertical position, and a piece of rubber tubing attached to the adapter. The cylinder valve is then opened and carefully regulated, so as to give a steady and not too rapid current of the gas, and the rubber tube is connected with the tap *a*, which is turned so that the gas enters the tube A, driving out the contained air through the tap *b*. After a minute the tube A will be filled with the gas; the operation may, however, be continued until needle-shaped crystals of potassium bicarbonate are formed in the upper narrow portion of A. The tap *b* is then closed, and after the gas in A has been brought to atmospheric pressure by removing the rubber tubing, the tap *a* is turned through 90° to bring A and B into communication. The potassium hydroxide solution immediately rises in A; the absorption may be hastened by gradually turning A into a nearly horizontal position. Towards the end of the absorption the tube is tilted to and fro and then clamped. The bottle D is then raised until the levels of the liquid in A and D are the same, and the volume of the gas read. When many determinations have to be made, the adjustment with D may be dispensed with and the volume read directly by the aid of a suitable correction table. The difference between two successive tests should not exceed 0·05 per cent. by volume. The upper part of the tube being graduated in $\frac{1}{20}$ c.c., it is possible to approximate to $\frac{1}{100}$ c.c. in the readings, and so obtain very accurate results.

To draw a sample from the liquid contents of the cylinder, it should be laid on its side, on a suitable support, so that the outlet tube of the valve points upwards. As a rule, it will be found possible to obtain a satisfactory and not too violent current of gas by slowly and cautiously opening the valve; small particles of solid carbonic acid will always be found to issue with the gas. In some cases the setting of the valve is very troublesome and the current of gas is so violent and intermittent that a very slight turning of the valve may cause the rubber

tubing to burst. When this is the case a reducing valve may be inserted and the gas allowed to issue for some considerable time to replace the air in the reducing valve completely before the sample is taken.

The methods for the examination of liquid carbon dioxide have been more recently investigated by Thiele and Deckert,[1] who have pointed out the importance of determining the gases other than carbon dioxide, and the difficulty of doing so if the carbon dioxide is determined by a gas-volumetric process, owing to the small volume of the residue. They accordingly recommend a method in which the carbon dioxide is absorbed over potassium hydroxide in a special measuring tube, fitted into a flask, which is weighed before and after the absorption. A considerable volume of the unabsorbed gases is thus obtained, which is transferred to a gas-volumeter for measurement and subsequently analysed if desired; the increase in weight of the flask gives the content of carbon dioxide.

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THE CHLORINE INDUSTRY

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and the late Professor G. LUNGE.

RAW MATERIALS

THE raw materials employed in the Weldon process and for the preparation of chlorine on a small scale, are hydrochloric acid, the examination of which has already been described (p. 514), and native manganese peroxide; the latter is necessary in the Weldon process to make good the loss of manganese that occurs in the operations involved. In the Deacon process hydrochloric acid is the only raw material; in the various electrolytic processes the raw material is either sodium chloride or potassium chloride.

In the Weldon process for regenerating the manganese dioxide, lime, or milk of lime, is required. The lime employed is very frequently prepared by burning limestone in the works where it is used. Certain special properties are essential in lime intended for this purpose. Slaked lime is also required in the manufacture of bleaching powder and milk of lime in the manufacture of potassium chlorate. The method of examining the potassium chloride employed in the latter industry is given in the section on "Potassium Salts" (Vol. II.) This section is restricted to the methods employed for the examination of manganese ore, quick lime, slaked lime and milk of lime.

I. MANGANESE ORE

Native manganese ore consists of manganese dioxide admixed with larger or smaller quantities of impurities. A description of the various minerals in which it is present, the localities in which they occur, etc., will be found in Lunge's *Sulphuric Acid and Alkali*.[1]

The technical examination of manganese ore intended for use in Weldon stills, is confined to the determination of moisture, active oxygen, carbon dioxide, and the quantity of hydrochloric acid necessary for decomposition.

[1] Vol. iii., p. 339.

1. **Moisture.**—According to R. Fresenius, manganese ore only parts with the whole of its hygroscopic moisture at 120°; at higher temperatures a portion of the combined water is also driven off. The method of drying recommended by Fresenius based on this consideration is, however, not followed in works, the practice being to dry the ore at 100° in the following manner.

A fair quantity of the very finely ground ore is weighed off, and spread out in a thin layer on a large watch-glass, and heated directly on a briskly boiling water-bath, or at 100° in a drying-oven, until the weight is constant. Drying should be complete after four hours; if it be continued for six hours, it is safe to assume that constant weight has been attained.

2. **Active Oxygen** is always expressed as percentage by weight of manganese dioxide. This includes all oxygen combined to form oxides higher than manganous oxide, MnO; or in other words, all oxygen capable of reacting with hydrochloric acid to liberate chlorine. One part active oxygen = 5·433 parts MnO_2.

Of the many methods of determination which have been proposed, only a few are actually employed. A method formerly much used is that of Berthier and Thompson, as modified by Fresenius and Will, which depends on the oxidation of oxalic acid.

The ore is warmed with strong sulphuric acid and oxalic acid, the carbon dioxide liberated thoroughly dried before leaving the apparatus, and the loss of weight determined. There are many sources of error, only partly overcome by the proposal to weigh the carbon dioxide directly by absorbing it with soda lime.

Better results are obtained by applying the reaction volumetrically, by starting, for example, with a known weight of oxalic acid and titrating back the excess with permanganate solution; this modification [1] has not, however, found any extended application in works practice.

The same may be said of Bunsen's method, which consists in boiling the ore with strong hydrochloric acid, absorbing the evolved chlorine in potassium iodide solution, and titrating the liberated iodine with sodium thiosulphate. This method is but seldom employed, notwithstanding the fact that the labour involved has been greatly reduced by the introduction of convenient apparatus.[2]

The method most generally adopted is the ferrous sulphate method of Levol and Poggiale. Carried out in the following manner described by Lunge, the process is looked upon as a standard method in the heavy chemical trade, as it is convenient and exact, and gives concordant results in the hands of different analysts.

[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 344.

[2] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 346, and Farsoe, *Z. anal. Chem.*, 1907, **46**, 308.

1·0866 g. of the very finely ground ore thoroughly dried at 100° is treated in a round-bottomed flask fitted with a Bunsen valve, or still better with a Contat bulb (Fig. 20, p. 63), with 75 c.c. of acid ferrous sulphate solution which is added from a pipette in three portions of 25 c.c. at a time. The ferrous sulphate solution is prepared by dissolving 100 g. of pure ferrous sulphate and 100 c.c. of pure concentrated sulphuric acid in 1 litre of water; it should be standardised daily when in use with $N/2$ permanganate solution, using the 25 c.c. pipette employed in the tests. After the addition of the ferrous sulphate solution, the flask is heated until the whole of the manganese dioxide has gone into solution and the insoluble residue is no longer dark coloured. When the flask and contents are quite cold the solution is diluted with from 100 to 200 c.c. of water, and titrated with permanganate until the faint rose-tint ceases to disappear instantaneously on stirring the solution, and remains permanent for at least half a minute; subsequent decoloration may be disregarded. The quantity of permanganate solution required is deducted from that corresponding to the 75 c.c. of ferrous sulphate solution; each 1 c.c. of the remainder corresponds to 0·02173 g. MnO_2, or for the weight of ore taken above, to 2 per cent. MnO_2.

Another method, characterised by extreme rapidity, and which is very useful as a check on the above, is Lunge's[1] gas-volumetric method, based on the interaction of peroxide of hydrogen and manganese dioxide according to the equation:—

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2.$$

The value of the peroxide is determined by the volume of oxygen evolved, which, as will be seen from the above equation, is equal to twice the quantity of "active oxygen" present in the manganese dioxide, the hydrogen peroxide being of course present in excess. Each 1 c.c. of oxygen evolved at 0° and 760 mm. corresponds to 0·003882 g. MnO_2. If 0·1941 g. of the manganese ore be taken for analysis, each 1 c.c. of oxygen evolved = 2 per cent. MnO_2; and if 0·3882 g. ore be taken, each 1 c.c. of oxygen = 1 per cent. MnO_2. The former quantity is suitable for small nitrometers, the latter for the larger apparatus.

The operation is carried out in the nitrometer with the auxiliary flask as described on p. 82, the volume of gas obtained being reduced to the volume of dry gas at 0° and 760 mm. It is, however, more convenient to employ the "Gas-volumeter" (p. 83), whereby the corrected volume is obtained without calculation.

The following points should be observed when carrying out this test. The ore must be ground until extremely fine, so as to allow of complete

[1] *Ber.*, 1885, 18, 1872; *Z. angew. Chem.*, 1890, 3, 8 and 75; *cf.* also, Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 349.

decomposition; and the quantity weighed off must be placed in the outer compartment of the decomposition flask, care being taken that none gets into the inner compartment. A few c.c. of dilute sulphuric acid is first added to decompose any carbonate present in the sample. Hydrogen peroxide is then placed in the inner compartment, an excess over the amount necessary to decompose the ore being used, and the bottle tightly closed by the rubber stopper connected with the nitrometer tap. The pressure is equalised by opening the tap to the air, so that the mercury comes to the zero point of the nitrometer. In placing the stopper in the decomposition flask, and also in the subsequent shaking, the flask should be held by the neck only, so as to avoid warming by the hand as far as possible: a more satisfactory plan is to allow the bottle to stand for at least ten minutes in water, at the room temperature, both before and after the decomposition. After the mercury has been brought to the zero mark the flask is tilted, so that the hydrogen peroxide flows from the inner compartment on to the ore, and the bottle is then shaken. Shaking should only be continued for two minutes (since after this period there is a risk of the insoluble matter acting upon the hydrogen peroxide and causing evolution of oxygen), even in cases where decomposition is incomplete owing to insufficient grinding. Incomplete decomposition is evidenced by the presence of dark material in the otherwise light coloured residue of silicate; longer agitation does not aid the reaction, but only promotes the decomposition of the peroxide. The level of the mercury should be adjusted and the volume of gas read as soon as the initial temperature has been attained.

The evolved gas may be regarded as fully saturated with aqueous vapour, and the reduction should be made by the aid of the "moist reduction tube" (p. 85); should the apparatus be provided with a "dry reduction tube," the correction must be carried out as described on p. 85.

A. Baumann[1] employs an azotometer for the decomposition (p. 75), and to avoid calculating the gas volume to 0° and 760 mm., weighs off a quantity of ore corresponding to the temperature and barometric pressure; this is facilitated by means of a table giving the quantity to be weighed off under varying conditions. The use of such a table does not allow of any variation in temperature between the time of weighing off the ore and the time of making the analysis, and since a difference of 1° C. means a rise or fall of 0·4 per cent. in the result this point is of considerable importance.[2]

A. Baumann[3] has also devised a volumetric method based on the same reaction. The manganese ore is allowed to react with an excess of hydrogen peroxide, previously standardised by permanganate solu-

[1] *Z. angew. Chem.*, 1890, 3, 78. [2] *Cf.* Lunge, *ibid.*, 136.
[3] *Ibid.*, 72.

tion, and the excess of peroxide is titrated back. The hydrogen peroxide solution employed is prepared by diluting the commercial peroxide with dilute sulphuric acid (1 : 10) until the mixture will decompose approximately its own volume of permanganate solution. For the analysis 0·4 to 1·0 g. of the very finely ground manganese ore is weighed off, and treated in a tall beaker or in a flask with exactly 50 c.c. of the hydrogen peroxide solution. The mixture is shaken at frequent intervals during half an hour, after which time any undecomposed hydrogen peroxide is titrated with permanganate solution.

MacLachlan[1] is of opinion that the determination of the active oxygen in hydrogen peroxide by means of an acid solution of potassium permanganate is altogether unreliable. Lunge maintains that this view only applies to the volumetric determination, and accordingly Baumann's method is to be regarded as inexact until further investigation proves the contrary. Lunge has fully confirmed the accuracy of the gas-volumetric method by a large number of tests.

For a critical discussion of the methods of determining available oxygen, see O. L. Barnebey.[2]

3. **Carbon dioxide.**—This determination is important, since carbon dioxide constitutes a very harmful impurity in chlorine intended for the manufacture of bleaching powder. Traces of carbonate may be detected by stirring the powdered ore on a watch-glass with water until all adhering air-bubbles have been removed, then adding a little dilute hydrochloric acid, and viewing the surface of the solution from the side. The liberated carbon dioxide comes off in the form of small, briskly evolved gas-bubbles, and cannot possibly be confused with air. The quantitative determination may either be carried out gravimetrically by liberating the carbon dioxide with dilute sulphuric or nitric acid, and absorbing in soda lime, or still better and more rapidly, by the gas-volumetric method described on p. 615. A good ore should not evolve more than 1 per cent. of carbon dioxide.

4. **The Hydrochloric acid necessary for decomposition.**—One g. of the ore is dissolved in 10 c.c. of strong works acid of known strength, the operation being carried out in a flask provided with a reflux condenser, and solution assisted by heating. The solution is then allowed to cool and normal sodium hydroxide added until the separated reddish-brown, flocculent precipitate of ferric hydroxide no longer dissolves on shaking. The number of c.c. of the acid used for decomposition, equivalent to the volume of sodium hydroxide solution required, is calculated, and the figure thus obtained deducted from 10, the number of the c.c. of acid taken in the first instance.

[1] *Chem. Soc. Proc.*, 1903, **19**, 216.

[2] *J. Ind. Eng. Chem.*, 1917, **9**, 961. *Cf.* O. L. Barnebey and G. M. Bishop, *J. Amer. Chem. Soc.*, 1917, **39**, 1235; and Barnebey and W. C. Hawes, *ibid.*, 607.

II. LIMESTONE

A description of the characteristics of the most suitable limestone for the manufacture of bleaching powder is given in Lunge's *Sulphuric Acid and Alkali*.[1] The properties required in lime intended for the Weldon process are somewhat similar; much depends in both cases on the absence of magnesia. The technical examination is carried out as follows:—

1. **Insoluble matter.**—One g. of the limestone is treated with hydrochloric acid, and the insoluble residue thoroughly washed, dried, and ignited. Should appreciable quantities of organic matter be present, the insoluble matter is first weighed on a tared filter paper, after drying at 100°, and then ignited; the difference between the two weighings gives the organic matter.

2. **Lime.**—One g. of the limestone is dissolved in 25 c.c. of normal hydrochloric acid and the excess of acid determined by titration with normal sodium hydroxide solution. The number of c.c. required is deducted from 25; the remainder multiplied by 2·803 gives the percentage content of CaO, or multiplied by 5·003, the percentage content of $CaCO_3$. This method of calculating the result gives any MgO present in terms of CaO, but this is quite permissible in limestones intended for use in alkali and bleaching powder works, since they should contain only very little magnesium oxide.

For the same reason, it is equally permissible to calculate the lime content from a determination of the carbon dioxide.

Should the limestone contain appreciable quantities of sesquioxides, these must first be removed by precipitation with ammonia (free from carbonate), and the calcium then precipitated as oxalate. In exact work the precipitates should be dissolved and reprecipitated (*cf.* p. 510). According to Passon,[2] this separation may be obviated by adding phenolphthalein to the acid solution of the limestone, and then sufficient ammonia to produce a distinct red coloration after precipitation is complete. A 10 per cent. solution of citric acid is then added until the colour disappears and the precipitate goes into solution, after which a further 10 c.c. of citric acid solution is added, the whole diluted with water, and the calcium precipitated by the addition of ammonium oxalate to the boiling solution. Iron, aluminium, magnesium, and phosphoric acid do not interfere when this method of precipitation is adopted.

3. **Magnesia** is, as a rule, only determined in limestone intended for use in the manganese recovery process, or in the manufacture of bleaching powder. Two g. of the sample is dissolved in hydrochloric acid, the calcium precipitated by the addition of ammonia and

[1] Vol. iii., p. 603. [2] *Z. angew. Chem.*, 1898, 11, 776.

ammonium oxalate, and the magnesium determined in the filtrate by precipitation with sodium phosphate (*cf.* p. 511).

4. **Iron** is usually only determined in limestone intended for the manufacture of bleaching powder. Two g. is dissolved in hydrochloric acid, the solution reduced by metallic zinc, diluted, and titrated with permanganate after the addition of manganese sulphate solution free from iron (*cf.* p. 452); or the solution may be reduced by stannous chloride, and the titration carried out with bichromate solution, after removing excess stannous chloride by means of mercuric chloride.

5. **Carbon dioxide** is very frequently determined by loss. Very many forms of apparatus for this purpose are in use.[1] The most rapid and accurate method is the gas-volumetric method described on p. 615. If 0·4497 g. of the sample be taken, each 1 c.c. of gas obtained, measured at 0° and 760 mm., corresponds to 1 per cent. $CaCO_3$.

III. Lime

A. Quick Lime

1. **Free Lime.**—One hundred g. of the average sample is weighed off, carefully slaked, and the resulting cream transferred to a 500 c.c. flask, which is then filled to the mark. One hundred c.c. of the thoroughly shaken contents is then drawn off with a pipette and diluted to 500 c.c. in a second flask, and 25 c.c. (= 1 g. quick lime) of the latter well-mixed solution taken for analysis. A small quantity of an alcoholic solution of phenolphthalein is first added and the solution then titrated with normal hydrochloric acid until the red coloration disappears. The colour change takes place when all the free CaO has been neutralised and before the $CaCO_3$ has been attacked. Each 1 c.c. of normal acid = 0·02804 g. CaO. The titration must be effected gradually, and with thorough mixing, otherwise accurate results cannot be obtained. The rapidity of the reaction is increased, and the clearness of the end-point improved, by adding 25 c.c. of a ten per cent. solution of barium chloride before beginning the titration.

Maynard[2] determines free caustic lime in admixture with other substances by extracting with pure glycerine at a temperature of 40°. The extraction is continued for five days in a thermostat, and the mixture frequently shaken. The whole is finally filtered at 60° and the lime determined in an aliquot part of the filtrate.

2. **Carbon dioxide.**—The CaO and $CaCO_3$ are titrated together by dissolving the lime in a measured volume of normal hydrochloric acid,

[1] *Cf.* Clowes and Coleman, *Quantitative Analysis*, 11th edition, 1918, p. 109; Treadwell, *Analytical Chemistry*, vol. ii., p. 375.

[2] *Bull. Soc. Chim.*, 1902 [3], **27**, 851; *Chem. News*, 1903, **87**, 109.

and titrating back the excess of acid with normal sodium hydroxide solution. The $CaCO_3$ present can then be calculated by deducting the value found for the CaO under test 1. In very exact work the carbon dioxide should be determined directly as described on p. 615.

B. Slaked Lime

1. **Water.**—About 1 g. of the substance is weighed off from a stoppered weighing bottle, and gradually heated to a red heat in a platinum crucible; it is then allowed to cool in the desiccator and weighed. The loss in weight = water + carbonic acid.

2. **Carbon dioxide** is determined as described above (A, No. 2).

3. **Content of milk of Lime in caustic Lime.**—*Blattner's specific gravity method.* In the case of a thin milk, the reading must be made quickly, and before the lime has time to settle out. In thicker milks, the hydrometer is placed gently in the solution, and the containing cylinder slowly rotated, so as to cause gentle shaking, until the hydrometer ceases to sink in the liquor. The cylinder employed should not be too narrow. The following table, reduced from that given by Blattner,[1] gives the relationship between lime content and specific gravity at 15° C.

Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.	Degrees Twaddell.	Grams CaO per litre.	Lbs. CaO per cubic foot.
2	11·7	0·7	28	177	11·1
4	24·4	1·5	30	190	11·9
6	37·1	2·3	32	203	12·7
8	49·8	3·1	34	216	13·5
10	62·5	3·9	36	229	14·3
12	75·2	4·7	38	242	15·1
14	87·9	5·5	40	255	15·9
16	100	6·3	42	268	16·7
18	113	7·1	44	281	17·6
20	126	7·9	46	294	18·4
22	138	8·7	48	307	19·2
24	152	9·5	50	321	20·0
26	164	10·3	...	...	...

CONTROL OF WORKING CONDITIONS

I. Manufacture of Chlorine by means of Native Manganese Ore

In this process analysis is confined to the determination of the free acid in the manganese liquors coming from the chlorine stills, by simple titration with normal sodium hydroxide solution, the end-point

[1] *Dingl. polyt. J.*, 1883, **250**, 464.

being decided by the appearance of a permanent, flocculent precipitate of ferric hydroxide. The residual acid in a well-finished liquor may be less than 5 per cent. in cases where the stills are heated indirectly; as a rule, the free acid rises to 6 per cent. and over, especially when the heating is done with open steam.

II. The Weldon Process

The finished liquors are examined in the following manner according to Lunge's modification of Weldon's method.

The liquors from the stills are tested for free acid as described above; with recovered manganese, such free acid should not exceed 1 per cent. Occasionally the liquors are also analysed for their manganese content, the method described under Weldon mud being employed (cf. *infra*).

The neutralised and settled liquors are tested for neutrality by means of litmus, and the degree of freedom from suspended matter judged by appearance; the percentage of calcium chloride present is determined by precipitation with oxalic acid in acetic acid solution.

The precipitated mud should further be repeatedly tested during oxidation, as a check on the blowing operation. The method of testing the mud is described below.[1]

The calcium chloride liquors which flow away from the settled mud are examined for freedom from mud carried forward mechanically.

The mud obtained from the settling-tanks or filter-presses must be examined for both soluble and insoluble manganese.

Hydrochloric acid used in the Weldon process should be as free as possible from sulphuric acid.

The Examination of Weldon Mud.

1. Manganese Dioxide.—For this determination the standard acid solution of ferrous sulphate is required, the preparation of which was described on p. 578. The ferrous sulphate solution gradually changes in value, and must therefore be checked from day to day.

The mud must be thoroughly shaken before testing (mere stirring is not sufficient), and 10 c.c. drawn off with a pipette before any settling has occurred. The outside of the pipette is freed from mud by washing, and the 10 c.c. of mud allowed to flow into 25 c.c. of the ferrous sulphate solution contained in a beaker, any particles adhering to the inner walls of the pipette being washed into the beaker by the aid of a wash-bottle. The mixture is then shaken until all the mud has dissolved, 100 c.c. of water added, and the solution titrated with $N/2$

[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 430.

permanganate. If the 25 c.c. of acid ferrous sulphate solution required x c.c. of permanganate, and the 10 c.c. of the mud and ferrous sulphate y c.c. of permanganate, then $2{\cdot}173\ (x-y)$ gives the number of grams of MnO_2 present in 1 litre of the mud, and $2{\cdot}173(x-y) \times 0{\cdot}0624$ the number of pounds per cubic foot.

2. **Total Manganese.**—Ten c.c. of the mud is measured off, observing the precautions described under test 1, and boiled with strong hydrochloric acid until chlorine ceases to be evolved. The excess of acid is then neutralised by addition of powdered marble or precipitated calcium carbonate, a strong filtered solution of bleaching powder added, the whole boiled for a few minutes until the colour becomes deep red, taking care that the mixture still smells of bleaching powder, when alcohol is added drop by drop until the red colour is destroyed. The whole of the manganese is then present as peroxide, which is filtered off and washed. The filtrate should be tested for freedom from manganese by adding bleaching powder solution, when no brown coloration should result. Washing is continued until the washings cease to give a reaction with iodised starch paper. The filter paper and precipitate are then added to 25 c.c. of standard ferrous sulphate solution, and dissolved by stirring as above. Should any of the manganese dioxide remain undissolved, a further 25 c.c. of the ferrous sulphate solution is added. The solution is diluted with 100 c.c. of water, and titrated with permanganate, the results being calculated as under test 1, and expressed as MnO_2 per litre or per cubic foot.

3. **The "Base,"** that is, the monoxides in the mud which neutralise hydrochloric acid but do not liberate chlorine, may contain lime, magnesia, ferrous oxide, and manganous oxide, and is expressed as the ratio of the number of molecules of these monoxides present to 1 molecule of manganese dioxide.

Ten c.c. of the well-shaken mud is added from a pipette to 25 c.c. (or 50 c.c. in the case of a very high base) of normal oxalic acid solution (63 g. cryst. oxalic acid per litre), previously diluted to about 100 c.c. and warmed to a temperature of 60° to 80°, and the mixture well stirred until the precipitate ceases to appear yellow and becomes pure white. This should not take long at the temperature specified. The solution is diluted to 202 c.c. (2 c.c. representing the volume occupied by the precipitate) in a suitably marked 200 c.c. flask, filtered through a dry pleated filter paper, and 100 c.c. titrated with normal sodium hydroxide solution. Tincture of litmus or phenolphthalein must be used as the indicator. The oxalic acid taken up by the mud serves (1) to reduce the MnO_2 to MnO with liberation of carbon dioxide; (2) to combine with and neutralise the manganous oxide so formed; (3) to saturate the monoxides, including manganous oxide originally present, that is, the "base." The quantities taken up

under 1 and 2 are equal, and the two together have the same numerical value as the MnO_2 as determined in test 1, and so equal $x-y$, since the oxalic acid solution is normal, whilst the permanganate solution is only semi-normal. If z c.c. of normal sodium hydroxide is used in titrating back the excess of oxalic acid, $25-2z$ c.c. of acid has been used altogether, and of this $x-y$ has been used by the manganese dioxide so that the substances under 3 correspond to 25 c.c. less $x-y$ and $2z$; therefore this value $w=25-(x+2z)+y$. The "base," then, is the ratio between w and $\frac{x-y}{2}$ (the sodium hydroxide solution being normal and the permanganate semi-normal); or $\frac{2w}{x-y}$. When 25 c.c. oxalic acid solution is used, it becomes:—

$$\frac{50-2x-4z+2y}{x-y} = \left(\frac{50-4z}{x-y}\right)-2,$$

or, when 50 c.c. oxalic acid is taken $= \left(\frac{100-4z}{x-y}\right)-2.$

III. The Deacon Process

In this process the ratio between hydrochloric acid gas and air must be determined both in the gases leaving the saltcake pot, and also in the gases leaving the Deacon decomposer.

In the gases from the saltcake pot it suffices to determine the volume percentage of hydrochloric acid gas present, as the residual gas is essentially air. This is effected by aspirating the gases through a measured volume of sodium hydroxide solution of known strength, coloured with litmus or with methyl orange until the indicator changes colour; the volume of non-absorbed gas (air) is ascertained by measuring the water which has run from the aspirator. Since the ratio of the volume of hydrochloric acid gas to the sodium hydroxide solution used is constant, and the volume of the air is given by the water collected, the ratio between the acid and the air is easily calculated. The principle of the method and the apparatus employed are the same as those described under Lunge's modification of Reich's method for the analysis of kiln gases (p. 398).

The gases leaving the decomposer are tested, as a rule, for free chlorine and for unchanged hydrochloric acid, and occasionally also for water vapour and for carbon dioxide.

1. **Ratio between the free Chlorine and the unchanged Hydrochloric Acid Gas** (*Decomposition value*). Simple absorption of the gases in sodium hydroxide solution followed by titration for available and total chlorine is not applicable in this case, since it is impossible

to avoid the formation of chlorate.[1] This difficulty has been overcome by the following method, devised in the works of Messrs Gaskell, Deacon, & Co.

Five litres of the gas leaving the decomposer is aspirated through 250 c.c. of sodium hydroxide solution of sp. gr. 1·075, divided between two or three bottles, to absorb both the hydrochloric acid gas and the chlorine. The apparatus should be fixed as near to the decomposer as possible, and the time during which the gas sample is taken should correspond with the period of working a charge through the saltcake pot. The contents of the several absorption bottles are united, diluted to 500 c.c., and tested as follows :—

1. One hundred c.c. of the solution is heated to boiling with 25 c.c. of the acid ferrous sulphate solution, prepared and standardised as described on p. 578. When cold, the contents of the flask are diluted with 200 c.c. of water, and titrated with $N/2$ permanganate solution. Let y represent the number of c.c. so required and x the number of c.c. of permanganate necessary to oxidise the 25 c.c. of ferrous sulphate solution.

2. A small volume of sulphur dioxide solution is added to 10 c.c. of the above alkaline solution and the mixture acidified with dilute sulphuric acid, so that there is a distinct smell of sulphur dioxide. The acidified solution is heated to boiling, allowed to cool, a few drops of permanganate solution added, if necessary, to oxidise any remaining sulphurous acid, after which the solution is neutralised with pure sodium carbonate, diluted with water and titrated with $N/10$ silver nitrate solution, employing neutral potassium chromate as indicator. Let z stand for the number of c.c. silver nitrate solution required. The percentage decomposition of the hydrochloric acid gas is then given by the expression $\frac{50(x-y)}{z}$, and the volume of air per 1 volume HCl by $\frac{45.0+\frac{x-y}{8}}{z}$. Should some other volume of gas, n, be aspirated instead of the 5 litres, the constant 45·0 must be altered to $\frac{1.641n}{50 \times 0.003645}$, assuming that the remaining operations are carried out exactly as above, and that 1 litre HCl at 0° and 760 mm. pressure weighs 1·641 gram.

Younger[2] passes the gas through a solution of arsenious acid and employs an aspirator which gives the weight of chlorine in unit volume of the gases directly. The percentage of hydrochloric acid in the gas is determined by titrating the resulting solution with silver nitrate. The absorption is effected in a cylinder containing 100 c.c. of an aqueous solution of arsenious acid, each 1 c.c. of which corresponds to 0·15432 grains (=0·01 g. chlorine). The charged cylinder is connected with the

[1] *Cf.* C. Winkler, *Industrie-Gase*, vol. ii., p. 318.

[2] *J. Soc. Chem. Ind.*, 1889, **8**, 88.

bottle B (Fig. 208), containing about 1 g. potassium iodide dissolved in water; the arsenious acid solution is coloured blue by a very small quantity of indigo-carmine.

A cubic foot (0·0283 cub. m.) in capacity of the aspirator C is divided into any convenient number of parts; for example, 112. One side of the gauge glass D is calibrated to give the grains of chlorine per cubic foot of gas, and the corresponding volume of gas aspirated is given on the other side of the same lines. The liberation of iodine from the potassium iodide solution and the simultaneous bleaching of the indigo-carmine indicate the completion of the test, and when this occurs the aspiration is interrupted and the readings taken. Thus, for example, if the mark E represents 1 cubic foot and the water stands at this level on the completion of the test, the readings indicate that 1 cubic foot of the gas contains 15·432 grains of chlorine. Should the water-level stand at the ½ cubic foot mark, the presence of 30·864 grains chlorine per cubic foot of gas is indicated by the scale, and so on.

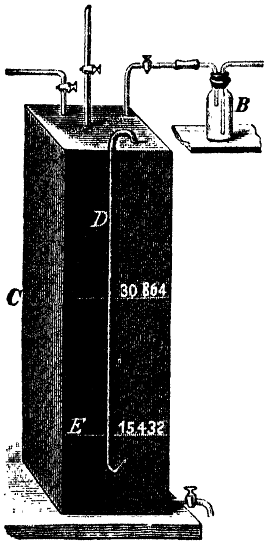

Fig. 208.

The hydrochloric acid is determined by titrating 10 c.c. of the arsenious acid solution with $N/10$ silver nitrate solution. Should the gases be free from hydrochloric acid the silver nitrate necessary for titration will be 28·2 c.c., this volume corresponding to the hydrochloric acid derived from the chlorine absorbed. Any volume over and above this 28·2 c.c. corresponds to the hydrochloric acid present as such in the gases.

The iodine liberated in the potassium iodide bottle generally indicates about 0·2 to 0·3 grains of chlorine. The potassium iodide bottle is not necessary as an indicator for the completion of the reaction; its main function is to show that the aspiration is not carried out too rapidly, and that no chlorine passes unabsorbed through the arsenious acid solution.

In a subsequent communication[1] Younger gives the following particulars for the analysis of Deacon gases: A measured volume of the gas is drawn first through weighed bottles containing concentrated sulphuric acid, the gain in weight giving the moisture present; secondly, through a tube containing a solution of arsenious acid, to arrive at the chlorine and hydrochloric acid content, as above; and finally, the oxygen in a sample of the gas from the aspirator is determined, the remainder of this gas being taken as nitrogen; thus the

[1] *J. Soc. Chem. Ind.*, 1890, 9, 159.

air (by calculation from the oxygen) and the excess nitrogen are obtained.

The following example, showing the methods of calculating the results, is taken from Winkler,[1] the data for the gases being corrected to the real litre weights. The free chlorine was determined by an arsenious acid solution, of which 1 c.c. = 0·0025 g. Cl, and the total chlorine by a silver nitrate solution, of which also 1 c.c. = 0·0025 g. Cl. The following volumes of these solutions were consumed per litre of unabsorbed gas. Fifty c.c. arsenious acid solution = $50 \times \cdot 0025 = 0\cdot 125$ g. free chlorine, and 100 c.c. silver nitrate solution = $100 \times 0\cdot 0025 = 0\cdot 25$ g. total chlorine. The extent of the decomposition is given by the equation :—

$$0.250 : 0.125 = 100 : x,$$
$$x = 50,$$

or a 50 per cent. decomposition had been effected. These two determinations thus give the decomposition value and the ratio between the chlorine and hydrochloric acid present in the gas.

Should it be desired to ascertain the volume percentage of the two gases leaving the Deacon decomposer, it is necessary to calculate to c.c. the ascertained weight of free chlorine, and of hydrochloric acid. One c.c. Cl = 0·003219 g., consequently the 0·125 g. Cl found correspond to 38·8 c.c. Cl, which is the volume present per 1 litre of non-absorbable gas.

To calculate the volume of the hydrochloric acid present, since its weight corresponds to half that of the total chlorine in the gases, it is,

$$= \frac{0.250}{2} = 0.125 \text{ g. Cl.} = 0.1285 \text{ g. HCl.}$$

One c.c. HCl weighs 0·001641 g. ; therefore :—

$$0\cdot 1285 \text{ g.} = 78\cdot 3 \text{ c.c. HCl}$$

per litre of non-absorbable gas. The *gas leaving the decomposer* has thus the following composition :—

1000	c.c.	oxygen and nitrogen,
78·3	„	hydrochloric acid gas,
38·8	„	chlorine ;

or, expressed in percentages by volume :—

89·52	vol.	per cent.	oxygen and nitrogen,
7·01	„	„	hydrochloric acid gas,
3·47	„	„	chlorine.

2. **The percentage by volume of Hydrochloric Acid Gas in the gases before entering the decomposer** is arrived at from the total chlorine as follows.

[1] *Industrie-Gase*, vol. ii., p. 317.

The total chlorine found, namely 0·250 g., corresponds to 0·257 g. or 156·6 c.c. HCl. Consequently the gases entering the decomposer correspond to:—

1000.0 c.c. air,
156.6 c.c. HCl,

which gives 13·60 volume per cent. HCl.[1]

It is usual to simplify the calculations as far as possible, and such simplification does not affect the result to any great extent. For example, the weight of 1 c.c. chlorine may be rounded off to 0·0032 g., and that of 1 c.c. HCl gas to 0·0016, that is, the weight of 1 c.c. HCl is taken to be one-half that of 1 c.c. of chlorine. If these simplifications be introduced in working out the above example, the following values are obtained:—

For the Gases leaving the Decomposer.

$$\frac{0.125 \text{ g. active chlorine}}{.0032} = 39.06 \text{ c.c.} = 3.49 \text{ vol. per cent. (instead of } 3.47)$$

$$\frac{0.125 \text{ g. inactive chlorine}}{.0016} = 78.12 \text{ c.c.} = 6.99 \text{ vol. per cent. (instead of } 7.01)$$

For the Gases entering the Decomposer

$$\frac{0.250 \text{ g. total chlorine}}{0.0016} = 156.25 \text{ c.c.} = 13.51 \text{ vol. per cent. HCl (instead of } 13.60).$$

It is unnecessary to make any corrections for temperature and pressure, since the errors from this source are throughout essentially of the same magnitude, and the results obtained are therefore sufficiently comparable.

3. Carbon Dioxide.—The determination of this gas is important in the examination of Deacon gases, since the presence of any appreciable amount in the chlorine renders the production of high-strength bleach impossible.

Hasenclever's method[2] of determination consists in passing a measured volume of the gas (previously freed from hydrochloric acid by bubbling through a wash-bottle containing water) through an ammoniacal solution of barium chloride. After the absorption is complete the solution is heated, the barium carbonate filtered off and thoroughly washed with boiled water. The washed precipitate is then either ignited and weighed, or dissolved in hydrochloric acid and converted into barium sulphate. The weight of carbon dioxide in the gas is calculated from the weight of precipitate obtained (1 g. $BaSO_4$ = 0.1885 g.

[1] This leaves out of account the oxygen which has interacted with the HCl, and assumes that here is no leakage into the decomposer (Conroy).

[2] *Cf.* Winkler, *loc. cit.*, p. 368.

CO_2), converted into volume, and compared with the volume of gas, say 20 litres, collected in the aspirator.

According to Sieber,[1] this method is only applicable to dilute gases containing not more than 10 per cent. of chlorine, a condition always satisfied by Deacon gases. In the case of more concentrated gases, such as electrolytic chlorine, which may contain carbon dioxide arising from the carbon electrodes used, the method is unsuitable, owing to the solubility of barium carbonate in barium chloride. The object of boiling the solution before filtering off the barium carbonate is to destroy any carbamate present in the liquid.

Another method is to absorb the gases in sodium hydroxide solution of known carbonate content, to decompose the sodium hypochlorite by boiling with cobalt oxide, and then to treat with sulphuric acid, passing the liberated carbon dioxide through a solution of potassium iodide previously saturated with carbon dioxide and air, to retain any traces of chlorine carried forward. The purified gas is then collected in a cooled potash bulb, and weighed; but Lunge[2] remarks that the gas must, of course, be dried beforehand, and that the process, in addition to being very complicated, is quite unreliable for the determination of small quantities of carbon dioxide, especially on account of the necessity of working with a solution of potassium iodide saturated as above. It is both simpler and more accurate to absorb the gas in sodium hydroxide solution, to decompose the hypochlorite completely by boiling with ammonia, and then to estimate the carbon dioxide in the ordinary way either by liberating the gas (p. 615) or by the barium chloride method.

4. **Moisture** in the Deacon gases may be determined when necessary by inserting a U-tube filled with pumice moistened with concentrated sulphuric acid, or a bulb apparatus containing sulphuric acid, between the gas main and the absorbing bottle for the chlorine and hydrochloric acid, and determining the gain in weight. It is essential to drive all chlorine and hydrochloric acid gas out of the absorbing tube before weighing, by passing a current of dry air through the U-tube for a sufficient time; also it is advisable to insert a second weighed sulphuric acid tube behind the drying apparatus during the operation. (Compare Younger, p. 588.)

IV. Electrolytic Chlorine[3]

It is necessary to avoid the formation of hydrochloric acid, which takes place when the electrolytic chlorine is exposed to light. A sample of gas containing originally 83·6 per cent. of chlorine and 3·6

[1] *Chem. Zeit.*, 1895, 19, 1963. [2] *Handbuch der Sodaindustrie*, vol. iii., p. 698.

[3] For much of the content of this section, the reviser is indebted to Mr James M. Taylor, of the United Alkali Co.'s Central Laboratory, Widnes.

per cent. of hydrogen had almost the whole of its hydrogen converted into hydrochloric acid during thirty seconds' exposure to April daylight at noon. This can be prevented by the use of amber glass, or by covering the glass pipette with a dark cloth. The rubber connection to the pipette should be as short as possible, as hydrochloric acid is one of the products of the action of chlorine on rubber.

1. **Determination of Chlorine, Hydrochloric Acid, and Carbon Dioxide.** (Mercury method.)—A gas pipette of known capacity (about 200 c.c.), with well-fitting taps of not too small bore, is connected by 3 feet of stout rubber tubing to a levelling bottle containing mercury. The pipette is then filled with mercury and the upper tap closed. The levelling bottle is then lowered and the mercury runs out, leaving a vacuum in the pipette; the lower tap is then closed.

The pipette is now connected to the gas main and the gas allowed to fill it. The sample having been taken, a small amount of mercury is allowed to run in by the lower tap and well shaken to promote absorption of the chlorine. Mercury is alternately admitted and shaken until finally no further contraction takes place.

The gas pipette is placed on a stand, preferably on a split ring covered with rubber, and connected to a Bunte burette (see p. 278) filled with mercury. The gas is transferred to the burette, the operation being complete when mercury shows in the capillary. The gas is brought to atmospheric pressure by means of the levelling bottle, and the lower tap closed. The burette is read, the mercury bottle lowered, and about 1 c.c. of mercury run out. This enables one to draw in the soda for the absorption of the carbon dioxide. The gas is brought to atmospheric pressure by slowly running out mercury, the upper tap being kept open until the cup is just empty. This avoids any levelling with mercury and allowances for the height of soda. The burette is allowed to drain and the volume read off. The difference between the two readings gives the volume of carbon dioxide present in the gas.

Any hydrochloric acid left after absorbing the chlorine with mercury can be dissolved by the addition of four or five drops of water to the pipette, and shaking before transferring the gas. After the residual gas has been transferred to the Bunte burette, the mercury is run out of the pipette, which is then rinsed out with neutral distilled water and the calomel and pinhead mercury filtered off. The acidity is titrated with *N*/10 soda, using methyl orange as indicator. The amount of hydrochloric acid is usually so small that it will not affect the carbon dioxide results, and it need only occasionally be determined.

The two methods which follow are rapid, and give results comparable among themselves for works purposes; but they should be

compared from time to time with, and their results checked by, the mercury method.

2. Determination of Carbon Dioxide. (Hydrogen peroxide method.)—This method depends on the following reaction :—

$$Cl_2 + H_2O_2 = O_2 + 2HCl$$

so that one volume of chlorine gives one volume of oxygen. If, therefore, 100 c.c. of electrolytic gas be treated with a solution of hydrogen peroxide the volume remains the same, but the water-soluble chlorine is converted into oxygen. Carbon dioxide can then be extracted by dilute soda.

A Bunte or Robinson burette, holding 104 to 105 c.c., is filled with good tap water, using an inverted wash-bottle with a length of rubber tube previously filled with water. It is inverted and connected to the chlorine main, and as the water runs out the gas fills the burette. The bottom tap is closed, and then the upper tap. Water is again introduced through the bottom tap until it just reaches the 100 c.c. mark, the upper tap being open meanwhile to ensure the gas being at atmospheric pressure.

(*Note.*—If the available burette contains 100 c.c. from tap to tap, 4 c.c. of water should be introduced, as it is necessary to have liquid in the burette, otherwise gas will escape when the bottom tap is opened. The result must then be divided by 0·96 to get percentages by volume. To ensure the gas being at atmospheric pressure, the momentary opening of the upper tap when the cup is empty will suffice. It is usually advisable to open the lower tap and allow some of the liquid to run out before adding reagents through the cup. This produces a slightly lower pressure inside the burette, sufficient to draw some of the reagent into it. The upper tap should be wide open, and the rate of flow be regulated by the lower tap until the cup is just empty. The gas then being at atmospheric pressure, the upper tap is shut and the burette allowed to drain.)

Eight to 10 c.c. of a 20-volume solution of hydrogen peroxide (6 per cent.), coloured with methyl orange, is poured into the cup and slowly drawn into the burette, wetting the sides uniformly. The speed is regulated by the lower tap, avoiding escape of gas from the first sudden evolution. To ensure the sides being wetted, it is advisable to take the burette out of the stand, and holding it horizontally by the ends (to avoid heating the body), to depress one end slightly and then the other. The see-saw motion is repeated seven or eight times, occasionally shaking the tube to wet the sides thoroughly. The conversion of the chlorine is complete when the pink colour remains. Should it be destroyed, 2 c.c. of peroxide is introduced, after relieving any pressure by opening the lower tap, and the gentle shaking repeated.

The burette is then replaced in the stand, and 4 or 5 c.c. of water poured into the cup and allowed to drain slowly down the sides. This displaces the peroxide, and prevents liberation of oxygen on adding sodium hydroxide. After draining 1½ or 2 minutes the volume of gas is read off.

Five to 10 c.c. of approximately normal sodium hydroxide is now poured into the cup and allowed to enter the burette and absorb the carbon dioxide. After bringing to atmospheric pressure the volume is read off. The difference is the volume of carbon dioxide present in the gas.

3. **Determination of Carbon Dioxide and Chlorine.** (Thiosulphate method.)—A 50 c.c. gas burette, graduated in c.c., with taps at each end, is filled with the sample to be tested. This can be done quickly by means of a rubber aspirator; three pulls should suffice to give a fair sample.

The end of the burette is then submerged in a 5 per cent. solution of caustic soda and the tap opened. Soda rushes in, absorbing the carbon dioxide and chlorine. The tap is shut and the tube shaken, to make certain that absorption is complete, when on opening the tap under the soda no further contraction takes place. The burette is held vertically and the height of the liquid noted: this figure multiplied by two gives the percentage of carbon dioxide and chlorine.

The same or a similar burette is filled with another sample of gas and the end submerged in a 10 to 20 per cent. solution of thiosulphate, which absorbs the chlorine: twice the diminution in volume is the percentage of chlorine.

No attempt is made to read the volumes at atmospheric pressure, but as it is the difference between two readings that is taken, the error is not very large.

Owing to the action of chlorine on thiosulphate being variable, and sulphur dioxide and sulphur monochloride being among the products, this method will only give correct results when the errors balance each other. Together with the peroxide method it affords a rough and quick method for the carbon dioxide determination.

4. **Determination of Oxygen, Hydrogen and Nitrogen.**—If the inert gas from 200 c.c. of electrolytic chlorine be too little for these determinations, a larger quantity of gas must be passed through caustic soda to absorb chlorine and carbon dioxide, and the residual gas analysed. The most convenient apparatus for this purpose is that described by Treadwell.[1] (Fig. 209.)

The filter flask A, of about 1·5 litres capacity, contains about 400 c.c. of caustic soda solution of sp. gr. 1·1. The absorption tube H is filled with the soda solution by suction at H, the cock I is turned into the position II, and the glass tube is filled with solution up to the cock by

[1] *Analytical Chemistry*, vol. ii., p. 812.

suction at the left arm. The cock is then turned to position I, the left arm connected to the gas-main, and gas drawn through by suction at the right arm of the cock till all air is expelled from the connecting tubing. The cock is again turned to position II, and by means of an aspirator at *a*, gas is slowly drawn into the absorption tube. Chlorine and carbon dioxide are absorbed, and the residual gas collects in the upper part of H. When enough has collected (50 to 70 c.c.), it is transferred to an Orsat or Hempel gas apparatus and measured. It is then sent into the soda pipette of the apparatus to make sure that the chlorine and carbon dioxide have been completely absorbed, and the oxygen, carbon monoxide, and hydrogen are determined in the usual way (see pp. 240 *et seq.*). Nitrogen is taken by difference, and, if desired, the equivalent oxygen to convert this into air can be calculated and the excess oxygen expressed as such.

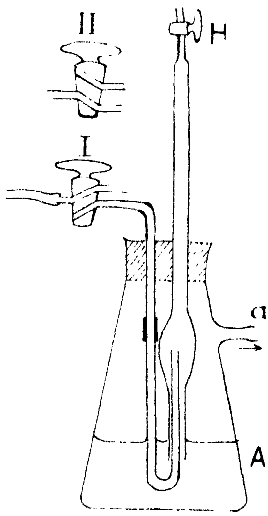

FIG. 209.

If only hydrogen is to be determined, the caustic soda in the absorption apparatus can be used many times; but where oxygen is to be determined fresh soda must be used for each test, as the sodium hypochlorite formed readily gives off oxygen on being kept.

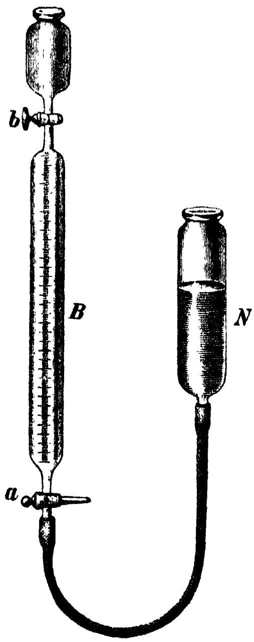

FIG. 210.

Treadwell[1] makes use of the burette shown in Fig. 210 for determining the carbon dioxide in electrolytic chlorine. The burette is of the Bunte type, and is provided with a levelling tube. The capacity of the burette, from tap to tap, must be accurately determined, the most suitable capacity being 100 c.c. The chlorine gas to be examined is dried by passing through a calcium chlorine tube, and is allowed to flow through the thoroughly dry burette for from five to ten minutes. The lower three-way tap *a* is now closed, then the upper two-way tap *b*, and the temperature and barometric height noted. The lower tap is then connected by the rubber tube to N, *a* is turned so as to connect N with the outside air, the tip of the burette and the stopcock are washed, and *a* is closed.

[1] *Analytical Chemistry*, vol. ii., p. 808; *Z. angew. Chem.*, 1905, **18**, 1930.

A potassium arsenite solution is made by dissolving 4·95 g. of arsenious oxide in dilute potassium hydroxide solution, adding phenolphthalein, exactly neutralising with sulphuric acid, and diluting to 1 litre. One hundred c.c. of this *N*/10 solution is placed in N, any air in the rubber tube is expelled by pinching with the thumb and finger, and the arsenite solution is introduced into the burette till all the chlorine is absorbed, after which 10 c.c. of a 1 : 2 potassium hydroxide solution is run in through the funnel above B, to absorb the carbon dioxide. After taking the readings, the solutions and washings are collected, phenolphthalein added, and the whole neutralised with hydrochloric acid; 60 c.c. of sodium bicarbonate solution (40 g. per litre) is then added, and the excess of arsenite solution titrated with *N*/10 iodine solution and starch. One c.c. *N*/10 solution = 0·003546 g. Cl, or 1·1015 c.c. at N.T.P. As the original gas was dry, the volume of the residual gas must, for accuracy, be corrected for aqueous vapour, and the volumes of chlorine found corrected from N.T.P. to the temperature and atmospheric pressure of the experiment. The carbon dioxide is then determined by difference.

Lunge and Rittener[1] absorb the chlorine in a Bunte burette with a *N*/10 solution of sodium arsenite and then the carbon dioxide with sodium hydroxide; the unchanged arsenite is titrated back and the carbon dioxide obtained by difference from the volume of total absorbable gases found. The details of the method are given on p. 615.

V. The Manufacture of Bleaching Powder

The method of examining the lime used in filling the chambers has already been described (p. 583). The main point to be attended to in the manufacturing operation is the strength of the bleach, which must be brought to a specified standard. This is controlled by analysis; the various methods available are described under "Finished products" (p. 600). It is, of course, essential that the sample drawn from the chamber should be representative of the bulk.

The chambers must not be opened until it has been ascertained that this may be done with safety to the workmen, and without giving rise to undue nuisance.[2] Before the chamber is opened, the chlorine present in the gas space must not exceed 5 grains per cubic foot (= 11·5 g. per cubic metre); this limit was agreed to by manufacturers about twenty years ago, but the present practice is to reduce the limit to 2½ grains per cubic foot.

The determination of the chlorine present in the chamber atmo-

[1] *Z. angew. Chem.*, 1906, **19**, 1853.

[2] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 622.

sphere may be carried out in an Orsat apparatus, the simplified form described by Fleming Stark,[1] Fig. 211, being especially suitable.

The burette *a* is filled with water and connected by means of a rubber tube with the reservoir *b*, a tap *c* being inserted between the two. This tap is provided with two passages at right angles to each other, the one of small and the second of large diameter. This arrangement allows of a strong flow of water when filling the burette, and of a diminished flow when the gas is forced into the absorbing solutions. The four tubes *d* are filled with an aqueous solution of potassium iodide, and each may be connected through a corresponding glass tap with the burette. Each absorption tube is provided with a double-bored stopper, and a tube reaching almost to the bottom of the absorption vessel passes through one of these openings. This tube is narrowed at its lower end, so as to break up the gas-bubbles entering the absorbing solution, and at its upper end is connected through the tube *e* with the bleaching powder chamber. The tube passing through the second opening in the stopper is cut off just below the stopper, and serves to connect the absorbing vessels with the burette. A small wash-bottle containing potassium iodide solution and starch is inserted between the absorption tubes and the burette. The two-way tap *g*, provided between the wash-bottle and the burette, permits the air to escape during the filling of the burette without passing through the wash-bottle.

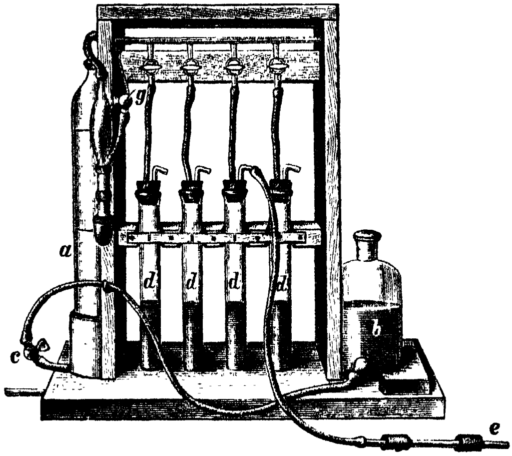

FIG. 211.

In using the apparatus, 387·7 c.c. of gas, as measured in *a*, are drawn through one of the absorption tubes *d*; the solution in the wash-bottle affords an absolutely safe indication of the completeness of the chlorine absorption. The contents of *d* are then washed into a beaker, and titrated with *N*/10 sodium arsenite solution. The grains of chlorine per cubic foot are obtained by multiplying by 2 the number of c.c. of arsenite solution so required.

The Government inspectors make use of the simple apparatus shown in Fig. 212.[2] A is an ordinary rubber pressure ball of about

[1] *J. Soc. Chem. Ind.*, 1885, 4, 311.
[2] Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 622.

100 c.c. capacity, provided with a small hole, B, in the mouthpiece. The end of the mouthpiece passes through one of the two holes in the cork C, a glass tube, D, bent at right angles passing through the second. This latter tube reaches nearly to the bottom of the cylinder E, and is narrowed down at the lower end, so that only a very fine needle can be inserted. The cylinder E is filled with the solution described below, and the outer end of D is inserted in an opening in the bleach chamber at a height of 2 feet above the floor. To take a sample of the chamber gas, A is compressed; the hole B is then covered by the finger and the pressure released; by the expansion of the bulb the gas in the chamber is drawn through the tube D and the solution in E. The operation is repeated until the solution in E becomes coloured through separation of iodine, and the number of aspirations required to cause this is noted. Each delivery of the bulb corresponds to 4 ozs. (about 100 c.c.), or $\frac{1}{250}$ of a cubic foot. The solution employed is prepared by dissolving 0·3485 g. of arsenious acid in sodium carbonate, neutralising with sulphuric acid, adding 25 g. of potassium iodide, 5 g. of precipitated calcium carbonate, 6 to 10 drops of ammonia, and diluting the whole to 1 litre. Twenty-six c.c. of this solution is employed for each test, and a little starch solution is added as indicator. Under these conditions five deliveries of the bulb will produce a coloration when the gas contains 5 grains of chlorine per cubic foot, ten deliveries when the chlorine content is only $2\frac{1}{2}$ grains per cubic foot, and so on.

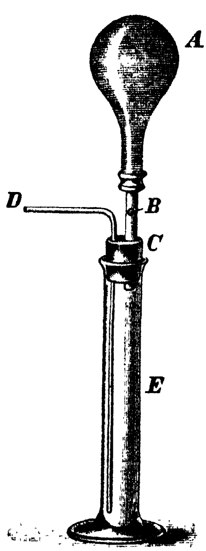

FIG. 212.

VI. THE MANUFACTURE OF POTASSIUM CHLORATE

In the old process of manufacture, in which a warm solution of milk of lime is treated with chlorine, the methods of examining the lime and milk of lime are those already described (p. 582). The resulting liquor must be examined for its content of chlorate, since this is the basis on which the potassium chloride necessary for conversion into chlorate is calculated, and also for the percentage of calcium chloride present, as a check on the working of the process.

Determination of the Chlorate.—Two c.c. of the liquor is measured off with an accurate pipette and boiled, after the addition of a little hot water and a drop of alcohol, to remove any dissolved free chlorine. A flask fitted with a Bunsen valve or Contat bulb (Fig. 20, p. 63) is used for the test, but the valve is not inserted during the above preliminary

heating. The complete removal of chlorine is indicated by the disappearance of all smell of chlorine and of the red colour. The flask and contents are allowed to cool, 25 c.c. of the acid ferrous sulphate solution (corresponding to a c.c. $N/2$ permanganate solution) described on p. 578 added, the whole boiled for ten minutes, and the valve inserted. When cold, the solution is titrated with $N/2$ permanganate solution, b c.c., say, being necessary to produce the coloration. The chlorate contained in 1 litre of the liquor will then be $5 \cdot 105\ (a-b)$ g. calculated as $KClO_3$, and the potassium chloride theoretically necessary to convert the calcium into the potassium salt will be $3 \cdot 106\ (a-b)$ g. per litre.[1]

The chlorate remaining in the mother liquors is similarly determined.

The chlorate may also be determined by Bunsen's method, namely, boiling with strong hydrochloric acid and absorbing the liberated chlorine in a solution of potassium iodide; the method is, however, no more advantageous in this case than in that of manganese ore (p. 577).

Other methods for the determination of chlorates are described on p. 612.

Calcium Chloride.—The chloride (calcium chloride) in the liquors is determined as follows:—1 c.c. of the liquor is treated as above, to destroy free chlorine, until the red colour disappears, a little neutral potassium chromate added, and the solution titrated with $N/10$ silver nitrate solution, as described on p. 73. Each 1 c.c. of the silver nitrate solution corresponds to chlorine equivalent to 7·46 g. KCl, or 5·59 $CaCl_2$ per litre.

Should it be necessary to determine the *free chlorine* and *hypochlorite* present in the liquor, a measured volume of the liquor is allowed to flow into an excess of potasssium iodide solution and the iodine liberated determined by titration with thiosulphate. It is not permissible to add sodium carbonate to fix the chlorine before adding the potassium iodide, since, owing to the formation of iodic acid and the oxidation of the thiosulphate, too much iodine is then required.[2] The "bleaching chlorine" may, however, according to Pontius, be titrated directly with potassium iodide solution after addition of sodium bicarbonate (*cf.* p. 603).

The titration may also be carried out by Penot's method, described under bleaching powder, by addition of sodium arsenite solution, until a drop of the titrated liquor ceases to produce a blue colour on potassium iodide starch paper; or the arsenite solution may be added in excess and titrated back with iodine solution (*cf.* p. 604).

[1] *Cf.* also, Rosenbaum, *Z. angew. Chem.*, 1893, **6**, 80.
[2] Friedheim, *Z. anorg. Chem.*, 1893, **4**, 145.

FINISHED PRODUCTS

I. Bleaching Powder

Owing to the unstable nature of this substance, very special attention must be given to the collection and preservation of the samples. Exposure to air and to daylight is very prejudicial; exposure to sunlight still more so. The samples are drawn from the separate casks by a suitable auger (p. 10), and placed one after the other in a wide-mouthed bottle, which must be closed immediately after each portion has been introduced. The mixing and filling into the separate sample bottles, together with the sealing up of the latter, is performed as rapidly as possible in the manner prescribed on p. 10. The samples must be kept in a cool dark place prior to testing, and the tests should be made without delay.

The technical analysis of bleaching powder is confined to the determination of the "available" or "bleaching" chlorine, that is, of the compound $CaCl(OCl)$ which splits up into $Ca(OCl)_2$ and $CaCl_2$ on solution in water, and consequently shows the reactions of a hypochlorite. The quantity of available chlorine present is, in England and America, always expressed as percentage by weight on the bleaching powder, and the same method is usually followed in Germany and most other countries. In France, however, and to a certain extent in other countries, the strength is quoted in terms of Gay-Lussac degrees, which indicate the number of litres of chlorine gas, reduced to 0° and 760 mm., capable of being evolved from 1000 g. of bleaching powder. The following table shows the relationship between the English and French degrees:—

French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.	French Degrees	Per cent. Chlorine.	French Degrees.	Per cent. Chlorine.
63	20·28	77	24·79	91	29·29	105	33·80	119	38·31
64	20·60	78	25·11	92	29·62	106	34·12	120	38·63
65	20·92	79	25·43	93	29·94	107	34·44	121	38·95
66	21·25	80	25·75	94	30·26	108	34·77	122	39·27
67	21·57	81	26·07	95	30·58	109	35·09	123	39·59
68	21·89	82	26·40	96	30·90	110	35·41	124	39·92
69	22·21	83	26·72	97	31·23	111	35·73	125	40·24
70	22·53	84	27·04	98	31·55	112	36·05	126	40·56
71	22·86	85	27·36	99	31·87	113	36·38	127	40·88
72	23·18	86	27·68	100	32·19	114	36·70	128	41·20
73	23·50	87	28·01	101	32·51	115	37·02	...	...
74	23·82	88	28·33	102	32·83	116	37·34	...	...
75	24·14	89	28·65	103	33·16	117	37·66	...	...
76	24·47	90	28·97	104	33·48	118	37·99	...	...

The following table, prepared by Lunge and Bachofen,[1] gives the

[1] *Z. angew. Chem.*, 1893, 6, 326.

available chlorine corresponding to various specific gravities of bleaching powder solutions :—

Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.	Specific Gravity at 15°.	Available Chlorine. Grms. per litre.
1·1155	71·79	1·0800	49·96	1·0350	20·44
1·1150	71·50	1·0750	45·70	1·0300	17·36
1·1105	68·40	1·0700	42·31	1·0250	14·47
1·1100	68·00	1·0650	39·10	1·0200	11·41
1·1060	65·33	1·0600	35·81	1·0150	8·48
1·1050	64·50	1·0550	32·68	1·0100	5·58
1·1000	61·50	1·0500	29·60	1·0050	2·71
1·0950	58·40	1·0450	26·62	1·0025	1·40
1·0900	55·18	1·0400	23·75	1·0000	Trace
1·0850	52·27	...	...	...	...

Very many methods[1] have been devised for the determination of the available chlorine in bleaching powder, of which the following are the most important.

Gay-Lussac's Arsenious Acid Method.[2]—This, the oldest method, was introduced by Gay-Lussac in 1835, and is still in general use in France. It consists in treating the bleach with a hydrochloric acid solution of arsenious acid, prepared by dissolving 4·409 g. of arsenious acid in hydrochloric acid, and diluting with water to 1 litre. Ten c.c. of this solution is rendered blue by the addition of a drop of indigo solution, and titrated with a solution of bleaching powder until the blue colour disappears. The bleach solution is prepared by rubbing 10 g. of the bleaching powder with water and diluting to 1000 c.c. Since 0·04409 g. As_2O_3 corresponds to 10 c.c. of chlorine gas measured at 0° and 760 mm., to obtain the number of litres of chlorine gas corresponding to 1 kilo of bleach, it is only necessary to divide 1000 by the number of c.c. of the bleach solution required to decolorise the indigo solution. The results obtained vary considerably, according to the degree of dilution and the excess of acid present. Chlorine and arsenious acid can exist side by side in dilute solutions, and consequently the bleaching of the indigo is no indication that all arsenious oxide has been oxidised. Further, the coloration gradually becomes weaker as the titration proceeds, thus causing the end-reaction to be very indistinct.

On account of this gradual decolorisation, Denigés[3] replaces the indigo sulphate by potassium bromide, the end of the titration being indicated by the appearance of a distinct yellow colour. This indicator is also, according to Denigés, very suitable for titrating commercial

[1] *Cf.* Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 591.
[2] *Ann. Chim. Phys.* (2), 1824, **26**, 162 ; 1835, **60**, 225.
[3] *J. Pharm. Chim.*, 1891 [5], **23**, 101 ; *J. Chem. Soc.*, 1891, **60**, 615.

hypochlorite solutions (Eau de Javel) when these are coloured pink through presence of permanganate. In this case the small amount of permanganate present is first decomposed by the arsenious acid solution. The determination is carried out in the usual manner by adding a few drops of concentrated potassium bromide solution to 10 c.c. of the arsenious acid solution, and titrating this with the bleach solution until a permanent faint yellow coloration is obtained.

All methods of bleaching powder analysis must, according to general commercial practice, permit of the determination not only of the chlorine in the solution, but also of that present in the insoluble matter. The insoluble matter must be uniformly distributed through the solution so that the whole forms a uniform thin cream. Hence all methods in which the bleaching powder cream is run in from a burette are necessarily inaccurate, since the distribution of insoluble matter can never be uniform under such conditions. This source of error is avoided as follows.

The sample is prepared for analysis by triturating it with water to a thin cream. The grinding should be extremely intimate, and neither too much nor too little water should be used in the operation. The triturated cream should not contain so little water that the bleaching powder separates out again in lumps while being washed into the litre flask; if this does occur, more water must be added to the cream first prepared, and the whole again triturated for a short time in the mortar. When the operation has been properly performed, the cream will readily mix on shaking with the further water added in the litre flask.

Bunsen's Iodometric Method[1] depends on the separation of an amount of iodine equivalent to that of the available chlorine, when a bleach solution and potassium iodide are treated with hydrochloric acid. The iodine liberated remains dissolved in the excess of potassium iodide present, and is titrated with $N/10$ sodium thiosulphate solution (p. 69). If 1 g. of bleaching powder be taken for the titration, the percentage of available chlorine contained in the bleach is found by multiplying the number of the c.c. of thiosulphate required by 0·355. The titration should be performed rapidly to prevent loss of chlorine, and any considerable excess of hydrochloric acid must be avoided. It is best to prepare the cream with 1 g. of bleach and about 100 c.c. of water, and to add to this 2 to 3 g. of potassium iodide and about 10 drops of hydrochloric acid, and to stir once quietly with a glass rod so as to distribute the separated iodine evenly throughout the solution. The thiosulphate is then added rapidly and without stirring until the colour of the solution has been reduced to a faint yellow, starch solution added until the colour becomes deep blue, and the titration continued drop by drop to completion.

[1] *Annalen*, 1853, **86**, 265.

When carefully carried out, the method gives accurate results, but in no case are the results better than those obtained by Penot's method. The method is consequently but seldom employed in the works, more especially as the consumption of potassium iodide renders it expensive and Wagner's proposal to utilise the decolorised solutions as a solvent for the iodine is not practicable.

A very disturbing effect that frequently occurs in this method is a rapid reappearance of the blue colour; in impure solutions this often makes it impossible to determine the end-point of the reaction. R. Schultz[1] has found that this often happens in determining the excess of bleaching powder in disinfected waste liquors, and is to be ascribed to the presence of oxidising substances such as ferric oxide and calcium chlorate. According to Schultz, very satisfactory results may be obtained, if instead of hydrochloric acid, acetic acid be added to the mixed waste liquor, together with potassium iodide solution, and the resulting solution titrated with thiosulphate. In the case of strongly coloured liquors, the end-point is judged by comparing the colour of the titrated solution with that of the original, diluted to an equal bulk.

Bunsen's Distillation Method is even less acceptable[2] than the above for technical work. It consists in decomposing the bleaching powder with hydrochloric acid, in a flask, driving off the chlorine by boiling the mixture and passing the evolved gases into a solution of potassium iodide contained in an inverted retort, the liberated iodine being determined by titration. Any chlorate present in the bleach will liberate chlorine in this method.

Pontius' Potassium Iodide Method.[3]—This consists in titrating bleaching powder with potassium iodide solution after previous addition of sodium bicarbonate. 7·09 g. of bleach is dissolved in water in the usual manner and the cream diluted to 1000 c.c.; 50 c.c. of the solution, corresponding to 0·3545 g. of bleaching powder, is measured off, and about 3 g. of solid sodium bicarbonate added to and dissolved in the solution. One to 2 c.c. of starch solution is then added, and the solution immediately titrated (before the liberated hypochlorous acid can react with the starch solution) with $N/10$ potassium iodide solution until the coloration, which is at first reddish brown, and then blue, no longer disappears, and the colour becomes a bright and permanent blue. The reaction consists in the formation of potassium iodate from the mixture of hypochlorous acid, sodium bicarbonate, and potassium iodide:—

$$3CaOCl_2(=6Cl) + 6NaHCO_3 + KI = KIO_3 + 3CaCO_3 + 6NaCl + 3CO_2 + 3H_2O.$$

[1] *Z. angew. Chem.*, 1903, **16**, 833.
[2] *Cf.* Winkler, *Z. angew. Chem.*, 1903, **16**, 33.
[3] *Chem. Zeit.*, 1904, **28**, 59.

This process is also suited to the examination of bleaching solutions, the hypochlorous acid in this case being liberated by addition of boric acid. The method is especially applicable to the approximate determination of substances of quite unknown strength, and Lunge considers it more convenient for this purpose than Penot's method ; the latter is, however, more exact in all cases.

Penot's Arsenious Acid Method.—This method, which finds the greatest acceptance in practice, is both free from all sources of error, and easy to carry out.[1] The following details are as recommended by Lunge.

An alkaline solution of $N/10$ sodium arsenite is employed in place of the acid solution used in the Gay-Lussac method. The preparation of this solution has been described on p. 72. In alkaline solution the oxidation of arsenious to arsenic acid, which requires 4 atoms of chlorine per gram molecule, takes place smoothly and without loss of chlorine, the end-point of the titration being shown with extreme sharpness by the blue coloration produced on iodised starch paper. An excess of the arsenite solution may be added, and such excess titrated back with $N/10$ iodine solution, but this is seldom done, since it necessitates the use of two standard solutions and is in no way more accurate.[2]

In carrying out the test, 7·09 g. of the thoroughly mixed bleach samples is ground in a porcelain mortar with a little water to a uniform thin cream, diluted by addition of more water, and the whole washed into a litre flask and made up to 1000 c.c. The lip of the mortar should be greased on its under side with a little fat or vaseline, to facilitate the transference of the liquid from the mortar to the flask. Fifty c.c. of the thoroughly mixed solution (=0·3545 g. bleaching powder) is pipetted off and transferred to a beaker, where it is thoroughly stirred, whilst the $N/10$ arsenite solution is run in until nearly the full quantity expected to be required has been added. A drop of the solution is then placed on filter paper which has been moistened with a little potassium iodide starch solution. According to the depth of the blue colour obtained (in presence of larger quantities of chlorine a brown stain is produced), more or less additional arsenite solution is added and the spotting repeated until the test paper remains white, or until only a quite inappreciable coloration is produced. In making a duplicate titration, if the arsenite solution be added to within a few drops of the end (as indicated by the first titration), a little iodide and starch may be added to the solution and further arsenite added till the colour disappears; but if this addition be made too early, a false end-point may occur through the formation of iodine chloride. Each 1 c.c. of the arsenite required represents 1 per cent. of available chlorine in the sample.

[1] *J. prakt. Chem.*, 1896, **54**, 59.

[2] *Cf.* J. Clarens, *Compt. rend.*, 1914, **159**, 183.

Suitable iodised starch paper for this test is prepared as follows:—One g. of starch is boiled with 100 c.c. of water, the solution filtered and 0·1 g. of potassium iodide added to the filtrate. Filter paper is then soaked in this solution and dried on a porcelain or similar plate at 40° to 50°. For the spotting test the paper should be moistened, as the reaction is much cleaner and more delicate with moist than with dry paper. Three or four pieces of the paper are spread on a glass plate and any excess of water allowed to flow off; they are then ready for spotting. The disappearance of the blue colour may be very sharply determined if the paper is examined by transmitted light towards the end of the titration.

Lunge's Gas-volumetric Method.—Penot's method is so simple, convenient, and accurate, that no other method is really needed. It is, however, desirable to have an independent method, which may, when required, be used as a check. Lunge's gas-volumetric method serves this purpose. The hypochlorite is decomposed with hydrogen peroxide in a nitrometer or gas-volumeter, and the volume of the oxygen liberated measured. The reaction takes place according to the following equation:—

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

That is, the volume of active chlorine present is exactly equal to the volume of the oxygen liberated.[1] The operation is carried out in a nitrometer provided with a decomposition bottle, as in the analysis of manganese ore (*cf.* pp. 82 and 578). The addition of acid, as recommended by Vanino, is of doubtful value.[2]

The bleaching powder solution is advantageously prepared so that 25 c.c., the volume taken for the reaction, contains 1 g. of bleaching powder. This will be the case if 20 g. of the bleach is triturated with water as described above, and the resultant cream diluted with water to 500 c.c.; working with 25 c.c. of such a solution, each 1 c.c. of oxygen evolved, reduced to 0° and 760 mm., equals 0·3166 per cent. of chlorine. The test should be carried out with a bulb nitrometer graduated to 140 c.c. Should it be desired to work with a smaller nitrometer, say of 30 to 50 c.c. capacity, only 5 c.c. of the above solution should be taken, in which case each 1 c.c. of oxygen evolved will correspond to $5 \times 0{\cdot}3166 = 1{\cdot}583$ per cent. of chlorine. A still more convenient plan is to dissolve 7·915 g. of bleach in 250 c.c. of water, and to take 10 c.c. of the milky solution for the test; the percentage of available chlorine is then equal to the number of c.c. of oxygen liberated. A 50 c.c. instrument can be used under these conditions.

The hydrogen peroxide is introduced into the inner compartment of

[1] *Cf.* Lunge, *Chem. Ind.*, 1885, **8**, 168; *Ber.*, 1886, **19**, 868; *Z. angew. Chem.*, 1890, **3**, 8; Baumann and Vanino, *Z. angew. Chem.*, 1890, **3**, 80, 186, 509.

[2] *Z. angew. Chem.*, 1890, **3**, 136.

the decomposition bottle, and rendered just alkaline by the addition of a few drops of sodium hydroxide solution, to prevent the evolution of carbon dioxide; the bleaching powder solution is then placed in the outer compartment. The shaking should only be continued for from one to two minutes after mixing the solutions, and the volume of gas evolved should be read off immediately and before any spontaneous evolution of oxygen occurs. The addition of a considerable excess of sodium hydroxide to the peroxide must be avoided, but it is safe to add the hydroxide until the solution is distinctly alkaline and a flocculent precipitate appears. This addition should, of course, be made to each portion of peroxide immediately before the test. The hydrogen peroxide solution should not be too concentrated; 1 c.c. treated with excess of bleaching powder solution in the nitrometer should not give more than 7 c.c. total oxygen. If it is too strong, a little water may be added directly to the solution in the decomposing flask. A small excess of water is immaterial, and it also makes no difference whether the hydrogen peroxide is employed in considerable or only in small excess.

Baumann[1] has shown that in carrying out the gas-volumetric method with hydrogen peroxide it is very easy to obtain too high a result when the hydrogen peroxide solution has been kept in a stoppered bottle and has not been shaken before use, when the thorough shaking necessary in the analysis may give rise to the liberation of appreciable quantities of oxygen (from 0·5 to 2 mg. oxygen from 10 c.c. of hydrogen peroxide). This oxygen results from the continuous gradual decomposition of the peroxide and remains dissolved in the peroxide solution.

The fear that the solid particles present in the milky bleach solution might exert a catalytic influence, and thereby lead to high results, has proved to be groundless. The oxygen can be collected over mercury or water.

According to Lunge, the gas-volumetric method of testing bleach always gives higher results than are obtained by Penot's method. As the result of a very extended series of tests, he states that such excess of available chlorine amounts on the average to 0·15 or at most 0·2 per cent. The cause of this difference has not yet been definitely elucidated.

Vanino's Hydrogen Peroxide Method.[2]—This is a volumetric method for the analysis of bleaching powder based on the above reaction. The bleaching powder is decomposed by adding an excess of hydrogen peroxide, standardised by means of permanganate, and the undecomposed peroxide is titrated back. The method is more complicated than that of Penot, and offers no special advantages.

[1] *Z. angew. Chem.*, 1891, **4**, 450.

[2] *Z. angew. Chem.*, 1890, **3**, 83.

Vanino[1] recommends the following apparatus (Fig. 213) for the rapid approximate determination of available chlorine. It is very convenient, and is adapted for use by workmen in bleaching works, etc. It is also generally suitable for other tests in which an evolved gas is measured when rapid approximate results are wanted.

The bleaching powder is weighed off on a hand balance, rubbed to a cream with water, and introduced into the generating flask A; the

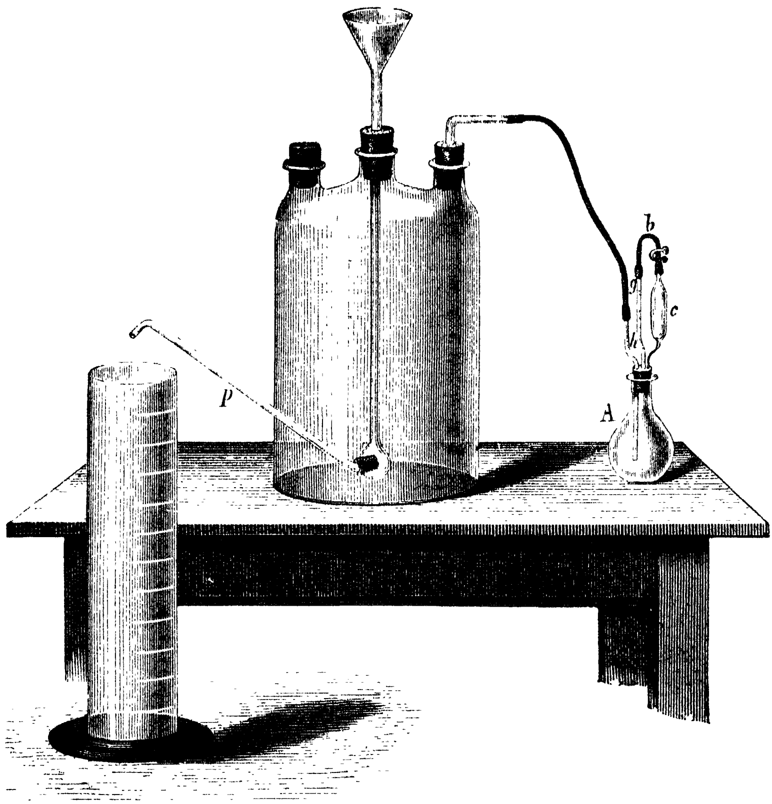

FIG. 213.

solution of hydrogen peroxide is placed in *c*. The outlet tube, *p*, of the gas-holder is best drawn out to a point, to reduce the tendency to form air-bubbles. The gas-holder is filled with water, and before each test the tube *p* is lowered so as to allow a few drops of water to escape; this tube must remain filled with water, both at the beginning and at the end of each experiment. A measuring cylinder is placed under the outlet of the tube *p*. By opening the pinchcock at *b*, the hydrogen peroxide solution flows into the bleach solution and the oxygen evolved displaces its own volume of water, which is collected in

[1] *Z. angew. Chem.*, 1890, **3**, 509. See also Müller, *ibid.*, 1910, **23**, 1556.

the measuring cylinder. A certain time is allowed to elapse after each test before the volume of water in the cylinder is read off. The results are calculated from Vanino's table (p. 609), the figures in which give the weight in milligrams of 1 c.c. of chlorine gas (saturated with moisture) at the temperatures and barometric pressures shown.[1] A deduction of 1 mm. must be made from the barometric reading at temperatures from 10° to 12°, of 2 mm. at 13° to 18°, and of 3 mm. at 20° to 25°, so as to reduce the reading of the barometer to 0°.

If, for example, 1·10 g. of bleaching powder is taken for the test and the volume of water collected, corresponding to the oxygen evolved, measures 140 c.c. at 10° and 720 mm. pressure, the calculation is made as follows. From the table the factor corresponding to 10° and 720 mm. is 2·858; this multiplied by 0·140, the volume of the water collected expressed in litres, gives 0·400 as the weight in g. of the chlorine contained in the 1·10 g. of bleaching powder, which, therefore, tests 36·36 per cent.

The *carbon dioxide* present in bleaching powder is occasionally determined. This may be done by decomposing the bleach with hydrochloric acid and passing the liberated chlorine and carbon dioxide into an ammoniacal solution of calcium chloride (one part $CaCl_2.6H_2O$, six parts water, and ten parts aqueous ammonia, sp. gr. 0·96, mixed and allowed to stand for some time). The chlorine reacts with the ammonia according to the equation :—

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The reaction may be hastened by boiling the solution. The carbon dioxide is converted into calcium carbonate, which is filtered off and determined in the usual manner.

The method devised by Lunge and Rittener (p. 615) is both more convenient and more accurate.

Orton and Jones[2] have devised a method for determining the alkalinity of bleaching powder solutions. A known volume of $N/10$ hydrochloric acid is placed in a Drechsel wash-bottle, a known volume of the bleach solution added, and dust-free air is bubbled through in a rapid stream in the dark till all the chlorine is evolved (till a drop of methyl orange is not bleached by the liquid). The excess of acid is then titrated by $N/10$ alkali. The reactions are :—

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2.$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

[1] This table is based on the value 3·16696 g. as representing the weight of 1 litre of dry chlorine at 0° C. and 760 mm. pressure, whereas the correct figure according to the most recent determinations is 3·214. Consequently, the whole of the values given in Vanino's table are 1·5 per cent. too low. Vanino has more recently (*Z. anal. Chem.*, 1902, **41**, 539) extended the table to 30° and for the odd values for the barometric pressure, within the above limits.

[2] *Analyst*, 1909, **34**, 317.

Barometric Pressure. Mm.	10°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	Barometric Pressure. Mm.
700	2·777	2·765	2·752	2·740	2·728	2·715	2·702	2·690	2·677	2·664	2·651	2·637	2·624	2·610	2·597	2·583	700
702	2·785	2·773	2·761	2·748	2·736	2·723	2·710	2·698	2·684	2·671	2·658	2·645	2·632	2·618	2·604	2·590	702
704	2·793	2·781	2·769	2·756	2·744	2·731	2·718	2·705	2·692	2·679	2·666	2·653	2·639	2·626	2·612	2·598	704
706	2·801	2·789	2·777	2·764	2·752	2·739	2·726	2·713	2·700	2·687	2·674	2·660	2·647	2·633	2·619	2·606	706
708	2·809	2·797	2·785	2·772	2·760	2·747	2·734	2·721	2·708	2·695	2·682	2·668	2·655	2·641	2·627	2·613	708
710	2·817	2·805	2·793	2·780	2·767	2·755	2·742	2·729	2·716	2·702	2·689	2·676	2·663	2·649	2·635	2·621	710
712	2·826	2·813	2·801	2·788	2·775	2·763	2·750	2·737	2·724	2·710	2·697	2·684	2·670	2·656	2·643	2·629	712
714	2·834	2·821	2·808	2·796	2·783	2·770	2·758	2·745	2·732	2·718	2·705	2·691	2·678	2·664	2·650	2·636	714
716	2·842	2·829	2·816	2·804	2·791	2·778	2·765	2·753	2·739	2·726	2·713	2·699	2·686	2·672	2·658	2·644	716
718	2·850	2·837	2·824	2·812	2·799	2·786	2·773	2·760	2·747	2·734	2·720	2·707	2·693	2·679	2·665	2·651	718
720	2·858	2·845	2·832	2·820	2·807	2·794	2·781	2·768	2·755	2·741	2·728	2·715	2·701	2·687	2·673	2·659	720
722	2·866	2·853	2·840	2·828	2·815	2·802	2·789	2·776	2·763	2·749	2·736	2·723	2·709	2·695	2·681	2·667	722
724	2·874	2·861	2·848	2·836	2·823	2·810	2·797	2·784	2·771	2·757	2·744	2·730	2·716	2·703	2·689	2·674	724
726	2·882	2·869	2·856	2·844	2·831	2·818	2·805	2·792	2·779	2·765	2·751	2·738	2·724	2·710	2·696	2·682	726
728	2·890	2·877	2·864	2·852	2·839	2·826	2·813	2·799	2·786	2·773	2·759	2·746	2·732	2·718	2·704	2·690	728
730	2·898	2·885	2·872	2·860	2·847	2·834	2·821	2·807	2·794	2·780	2·767	2·754	2·740	2·726	2·712	2·697	730
732	2·906	2·893	2·880	2·868	2·854	2·841	2·828	2·815	2·802	2·788	2·775	2·761	2·747	2·733	2·719	2·705	732
734	2·914	2·901	2·888	2·876	2·862	2·849	2·836	2·823	2·809	2·796	2·782	2·769	2·755	2·741	2·727	2·712	734
736	2·922	2·909	2·896	2·883	2·870	2·857	2·844	2·831	2·817	2·804	2·790	2·777	2·763	2·749	2·734	2·720	736
738	2·930	2·917	2·904	2·891	2·878	2·865	2·852	2·839	2·825	2·812	2·798	2·784	2·770	2·756	2·742	2·728	738
740	2·938	2·925	2·912	2·899	2·886	2·873	2·860	2·847	2·833	2·819	2·806	2·792	2·778	2·764	2·750	2·735	740
742	2·946	2·933	2·920	2·907	2·894	2·881	2·868	2·855	2·841	2·827	2·814	2·800	2·786	2·772	2·758	2·743	742
744	2·954	2·941	2·928	2·915	2·902	2·889	2·876	2·862	2·849	2·835	2·821	2·808	2·794	2·780	2·765	2·751	744
746	2·962	2·949	2·936	2·923	2·910	2·897	2·884	2·870	2·857	2·843	2·829	2·815	2·801	2·787	2·773	2·758	746
748	2·970	2·957	2·944	2·931	2·918	2·905	2·891	2·878	2·864	2·851	2·837	2·823	2·809	2·795	2·780	2·766	748
750	2·978	2·965	2·952	2·939	2·926	2·913	2·899	2·886	2·872	2·858	2·845	2·831	2·817	2·802	2·788	2·774	750
752	2·986	2·973	2·960	2·947	2·934	2·921	2·907	2·894	2·880	2·866	2·852	2·838	2·824	2·810	2·796	2·781	752
754	2·994	2·981	2·968	2·955	2·942	2·929	2·915	2·901	2·888	2·874	2·860	2·846	2·832	2·818	2·804	2·789	754
756	3·002	2·989	2·976	2·963	2·950	2·936	2·923	2·909	2·896	2·882	2·868	2·854	2·840	2·825	2·811	2·796	756
758	3·010	2·997	2·984	2·971	2·957	2·944	2·931	2·917	2·904	2·890	2·876	2·862	2·848	2·833	2·819	2·804	758
760	3·018	3·005	2·992	2·979	2·965	2·952	2·939	2·925	2·911	2·897	2·884	2·869	2·855	2·841	2·827	2·812	760
762	3·026	3·013	3·000	2·987	2·973	2·960	2·947	2·933	2·919	2·905	2·891	2·877	2·863	2·849	2·834	2·819	762
764	3·035	3·021	3·008	2·995	2·981	2·968	2·954	2·941	2·927	2·913	2·899	2·885	2·871	2·856	2·842	2·827	764
766	3·043	3·029	3·016	3·003	2·989	2·976	2·962	2·949	2·935	2·921	2·907	2·893	2·878	2·864	2·849	2·835	766
768	3·051	3·037	3·024	3·011	2·997	2·984	2·970	2·957	2·943	2·929	2·914	2·900	2·886	2·872	2·857	2·842	768
770	3·059	3·045	3·033	3·019	3·005	2·991	2·978	2·965	2·951	2·937	2·922	2·908	2·894	2·879	2·865	2·850	770

From the determination of the available chlorine, the amount of hydrochloric acid corresponding to the first equation is calculated, and that corresponding to the second is then obtained by difference.

M. Philibert[1] employs an iodometric method to determine the alkalinity of bleach solutions.

II. Bleaching Solutions and Electrolytic Liquors

Bleaching solutions consist essentially of mixtures of hypochlorites and chlorides, and some also contain free hypochlorous acid. The base may be calcium, potassium, sodium (in Eau de Javel and liq. sod. chlorinat.), or magnesium, zinc, etc. Whether such solutions be prepared by the double decomposition of bleaching powder with various salts, or by passing chlorine into milk of lime, sodium carbonate, etc., or by the electrolysis of chloride solutions, the constituents are hypochlorite, chloride, free hypochlorous acid, and chlorate, with bases such as the alkalis or calcium; the solutions may also contain carbonate in addition to caustic alkali.

The same constituents are present in the liquors which result from the electrolytic manufacture of caustic alkali or of chlorate, but the ratio between the various substances is very different from that existing in bleaching solutions. The same methods of analysis are, however, applicable in both instances.

James and Richey[2] have given a useful summary of the various methods of analysis adopted in electrolytic works.

Available Chlorine.—In bleach solutions the determination of the available chlorine is in most instances sufficient; this is carried out as described under bleaching powder (p. 600). For a rapid works method of determining available chlorine in bleaching liquors dependent on measurement of pressure of the oxygen evolved by the reaction of hydrogen peroxide on the liquor, see Schrero.[3]

The available chlorine may be due either to hypochlorites or to the free hypochlorous acid. The bleaching value is greater when the hypochlorous acid is free; and the exceptionally great bleaching value of many liquors, especially electrolytic liquors, depends on this, so that it may be necessary to determine the quantity of free hypochlorous acid accompanying the hypochlorite salts in solution. Insoluble substances or material remaining undissolved, such as zinc oxide, calcium hydroxide, etc., may be taken to be without action on hypochlorous acid. Should the liquor be found to contain free base in solution, free hypochlorous acid may be regarded as absent; it will only occur when all the basic material present has been saturated

[1] *J. Pharm. Chim.*, 1918 [vii.], **18**, 260.
[2] *J. Amer. Chem. Soc.*, 1902, **24**, 469.
[3] *J. Ind. Eng. Chem.*, 1921, **13**, 559; *J. Soc. Chem. Ind.*, 1921, **40**, 578 A.

by acid radicals. The various salts will, of course, be more or less hydrolytically or electrolytically dissociated according to the concentration of the solution, but such dissociation is without influence from the analytical standpoint.

Free Hypochlorous Acid.—If calculation should show that the quantity of base, the Na_2O, for instance, in the case of a soda solution, is insufficient to neutralise the whole of the acids found (to form sodium chloride, sulphate, carbonate, and hypochlorite), it may be concluded that free hypochlorous acid is present.

A much simpler method depends upon the fact that when a salt of hypochlorous acid reacts with potassium iodide, two molecules of the base are liberated, whilst free hypochlorous acid only sets free one molecule of the base:—

$$NaOCl + 2KI + H_2O = NaCl + 2KOH + I_2.$$
$$HOCl + 2KI = KCl + KOH + I_2.$$

Consequently, if the liberated iodine be removed by titrating the solution with thiosulphate, the two products can then be distinguished by titrating with standard acid. Any alkali carbonate present in the original solution must of course be allowed for (*cf.* p. 617).

The separation of free hypochlorous acid by distillation, with or without the addition of other acids, is too uncertain to be of value.

Lunge[1] has described a simple method for distinguishing between free chlorine and hypochlorous acid, based on their reaction with a neutral solution of potassium iodide; hypochlorous acid forms an alkali hydroxide, whilst in the case of chlorine the solution remains neutral, as shown in the following equations:—

$$1.\ ClOH + 2KI = KCl + KOH + I_2.$$
$$2.\ Cl_2 + 2KI = 2KCl + I_2.$$

In the first reaction the liberated iodine reacts with the potassium hydroxide to produce various compounds, especially potassium iodate; this may, however, be prevented by previously adding hydrochloric acid in known quantity to convert the free alkali into potassium chloride; it is then only necessary to titrate with standard alkali. The reactions in acid solution are:—

$$1a.\ ClOH + 2KI + HCl = 2KCl + I_2 + H_2O.$$
$$2a.\ Cl_2 + 2KI + HCl = 2KCl + I_2 + HCl.$$

That is, with hypochlorous acid one molecule of hydrochloric acid is neutralised for each molecule of hypochlorous acid reacting with potassium iodide, whilst in the case of chlorine the hydrochloric acid added remains unchanged. If, then, the solution be first

[1] *Chem. Ind.*, 1881, 4, 293.

titrated with $N/10$ thiosulphate solution, and then with $N/10$ sodium hydroxide solution, in 1*a* the volume of thiosulphate solution used will be equal to twice the difference between the number of c.c. of $N/10$ alkali necessary to neutralise the full quantity of acid originally added and that now required to neutralise the excess of free acid. In 2*a*, no such difference will occur. For intermediate cases it is easy to calculate the ratio between the hypochlorous acid and chlorine, since for each c.c. $N/10$ hydrochloric acid neutralised, 2 c.c. $N/10$ thiosulphate must be allotted to hypochlorite.

This method is difficult of application in the presence of free alkali or alkaline carbonate, but free chlorine is then hardly likely to be present.

Chlorates may be determined by first finding the available chlorine according to Penot's method, and then this and chlorate-chlorine together, by boiling with ferrous sulphate and titrating back the excess of the latter with permanganate, as described on p. 598. The difference between the two figures so obtained gives the chlorine present as chlorate. The chlorine present as hypochlorite and chlorate may also be determined iodometrically, by boiling with strong hydrochloric acid and collecting the evolved gas in potassium iodide solution (*cf.* p. 603).

According to Winteler,[1] the latter method is very inexact, but results accurate to within 0·1 to 0·2 per cent. are obtainable by the ferrous sulphate method, provided the solution containing the hypochlorite and chlorate be added to the measured excess of ferrous sulphate solution and the mixture be allowed to stand for several minutes before heating, air of course being excluded.

The direct method due to Fresenius[2] is preferable to the above, but more troublesome. The solution to be tested is treated with an excess of neutral lead acetate solution; a precipitate is formed which gradually turns brown with liberation of chlorine, and which contains a quantity of lead peroxide corresponding to the hypochlorite present:—

$$Ca(OCl)_2 + PbCl_2 = PbO_2 + CaCl_2 + Cl_2.$$

The solution is allowed to stand for eight to ten hours, with frequent agitation, until all smell of chlorine has disappeared. The chlorine liberated reacts with the lead acetate solution to form lead chloride, lead peroxide, and free acetic acid. The precipitate, consisting of the peroxide and chloride of lead, is filtered off and washed, the filtrate and washings concentrated by evaporation, and the contained lead and calcium precipitated by addition of sodium carbonate in slight excess; the filtrate, which then contains the chlorate as the sodium salt, is evaporated and its chlorate content determined (p. 598).

[1] *Z. angew. Chem.*, 1903, **16**, 33.

[2] *Ibid.*, 1895, **8**, 501.

For liquors which contain much hypochlorite together with chlorate, such as electrolytic and other bleaching solutions, Ditz and Knöpflmacher[1] recommended estimating the chlorate iodometrically by decomposition at the ordinary temperature with strong hydrochloric acid and potassium bromide. The process, which is also suitable for the examination of chlorate liquors, has been modified by Ditz[2] as follows. The apparatus employed is shown in Fig. 214. The bottle *a* has a capacity of about 1500 c.c., and may be closed either by the stopper *b*, or by the headpiece *c*, as shown in the figure. The latter is provided with a dropping funnel, *d*, and with an absorption tube, *e*.

The volume of chlorate solution used for a determination should contain approximately 0·1 g. of chlorate, calculated as $KClO_3$. In determining the chlorate in a mixture containing both chlorate and hypochlorite, the volume taken for analysis should be so regulated that the total consumption of $N/10$ sodium thiosulphate solution will be from 40 to 50 c.c. The measured volume of chlorate liquor, together with 10 c.c. of a 10 per cent. potassium bromide solution, is introduced into the bottle, and after the absorption tube has been filled to two-thirds of its height with a 5 per cent. solution of potassium iodide, concentrated hydrochloric acid is added from the dropping funnel *d*. If the volume of the chlorate solution does not exceed 25 c.c., 50 c.c. of acid is added, and proportionately more if more than 25 c.c. are required for the analysis. The liberated bromine is absorbed by the potassium iodide in *e*; to prevent the solution being sucked back into *a*, the stopper on the exit-tube of *e* is inserted. After the whole has been allowed to stand for five minutes, from 500 to 600 c.c. of distilled water are introduced through the dropping funnel, followed at a moderate rate by about 20 c.c. of the 5 per cent. potassium iodide solution. If more than 50 c.c. of hydrochloric acid have been used for the decomposition, proportionately more water must be added. The mixture is well agitated, the contents of the absorption tube blown over into *a*, the tube together with the headpiece thoroughly washed, the latter replaced by the glass stopper, and the liberated iodine determined

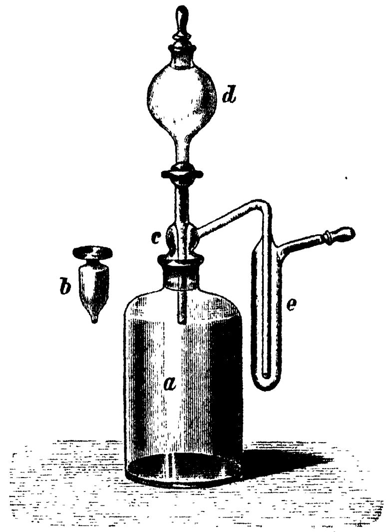

FIG. 214.

[1] *Z. angew. Chem.*, 1899, 12, 1195.
[2] *Chem. Zeit.*, 1901, 25, 727.

by titration with $N/10$ thiosulphate solution. If 1 c.c. of the thiosulphate solution equals a g. iodine and the volume required for the titration of the liberated iodine be b c.c., the weight of chlorate present is given by the equation:—

$$g\ KClO_3 = a \times b \times \frac{122{\cdot}60}{761{\cdot}8} = 0{\cdot}1609\ a \times b,$$

and the quantity of potassium chloride equivalent to this by the equation:—

$$g\ KCl = a \times b \times \frac{74{\cdot}60}{761{\cdot}8} = 0{\cdot}0979\ a \times b.$$

When examining mixtures containing both hypochlorite and chlorate, the quantity of hypochlorite present must be determined previously and allowed for.

Kolb and Davidson[1] also carry out the determination at the ordinary temperature. They dissolve about 0·08 g. of the chlorate in 10 c.c. of water, free from air, in a 500 c.c. flask, heat the solution on the water-bath, and allow it to cool in a current of carbon dioxide; 2 g. of potassium iodide and 50 c.c. of air-free hydrochloric acid of sp. gr. 1·12 are then added, the whole allowed to stand for an hour, protected from the light, diluted to 300 c.c. with boiled water saturated with carbon dioxide, and the liberated iodine finally titrated with sodium thiosulphate.

M. Scholtz[2] reduces the chlorate to chloride with nitric acid and sodium nitrite, adds a measured volume of $N/10$ silver nitrate solution, and titrates back the excess with ammonium thiocyanate, using ferric ammonium alum as indicator.

Hendrixson[3] reduces the chlorate with metallic iron, and titrates the resulting chloride, after oxidising the iron with nitric acid.

Knecht[4] runs 50 c.c. of titanous chloride solution (which must be kept in an atmosphere of hydrogen as described in the section on "Organic Dyes," Vol. IV.) into 5 c.c. of strong hydrochloric acid in a conical flask in an atmosphere of carbon dioxide. Then 10 c.c. of the chlorate solution (containing about 2 g. per litre) is run in from a pipette, and after at least three minutes thiocyanate is added, and the excess of titanous chloride is titrated by means of a standard solution of a ferric salt.

Chloride-chlorine.—The chlorine present as chloride is most con-

[1] *Z. angew. Chem.*, 1904, **17**, 1883; 1905, **18**, 1047, 1693. *Cf.* also Ditz, *ibid.*, 1905, **18**, 1518.
[2] *Arch. Pharm.*, 1905, **243**, 353; *J. Soc. Chem. Ind.*, 1905, **24**, 904.
[3] *Amer. Chem. J.*, 1904, **32**, 242.
[4] *J. Soc. Chem. Ind.*, 1908, **27**, 434; *New Reduction Methods in Volumetric Analysis*, 2nd edition, London, 1918.

veniently estimated in the following manner. The available chlorine is first determined by Penot's method (p. 604), whereby it is completely converted to chloride, whilst the arsenite is oxidised to sodium arsenate. The latter compound is an exceptionally good indicator for the silver nitrate titration, and it is unnecessary to make any deduction for the excess of silver nitrate necessary to produce the coloration. It is therefore only necessary nearly to neutralise the free alkali by cautious addition of nitric acid (a slight excess of alkali is not harmful, excess of free acid is) and then to titrate with silver nitrate solution, with good agitation, as described on p. 73, until the precipitate becomes red owing to the formation of a small quantity of silver arsenate. If preferred, the chloride may, of course, be determined gravimetrically. On deducting the chlorine corresponding to the hypochlorite and chlorate from the total chlorine as determined above, the quantity of chlorine present as chloride in the original solution is obtained.

Carbonic Acid.—In determining carbonic acid, the details given in describing the analysis of Deacon gases (p. 590) and of bleaching powder (p. 608) apply. Naturally, appreciable quantities of carbonic acid cannot exist in bleach solutions containing calcium oxide or magnesia; they may, however, be present in potash or soda bleaching solutions and in electrolytic potash and soda liquors. This carbonic acid may be determined by first converting the hypochlorite to chloride by boiling with ammonia solution free from carbonate, allowing the boiled solution to cool with exclusion of carbon dioxide, and then determining the total alkalinity by titrating a portion of the solution with methyl orange as indicator. The alkali hydroxide is determined in a second portion of the solution after addition of barium chloride, as described on p. 526. The difference between the two titrations gives the amount of carbonate present. The carbonic acid may also be obtained directly, after decomposing the hypochlorite in the manner described above, by liberating it with a strong acid and determining it either gravimetrically or gas-volumetrically (p. 82). Blattner's method (cf. *infra*) can also be used.

The determination of carbon dioxide in presence of chlorine can also be carried out by the simplified Lunge-Marchlewski method devised by Lunge and Rittener.[1]

The apparatus employed is shown in Fig. 215. The decomposition flask B has a capacity of about 30 c.c.; it is fitted with a tap-funnel C and capillary exit-tube D, which is cut off flush with the bottom of the rubber stopper in B. D is connected with the exit-tube of the Bunte burette A, as shown; the ungraduated portion of the burette must be calibrated.

[1] *Z. angew. Chem.*, 1906, 19, 1849.

To carry out a determination, sufficient substance or solution is introduced into B to evolve not more than 60 c.c. of gas; D is then connected with the burette, the taps E and F opened, and the whole evacuated by attaching an ordinary pump to F. This tap is then closed and connected with the pressure-bottle G, charged with saturated brine, which is used as the confining liquid in place of mercury. A little of the brine is allowed to enter the capillary portion of the bottom of the nitrometer, as a check on any possible leakage, and the tap F again closed.

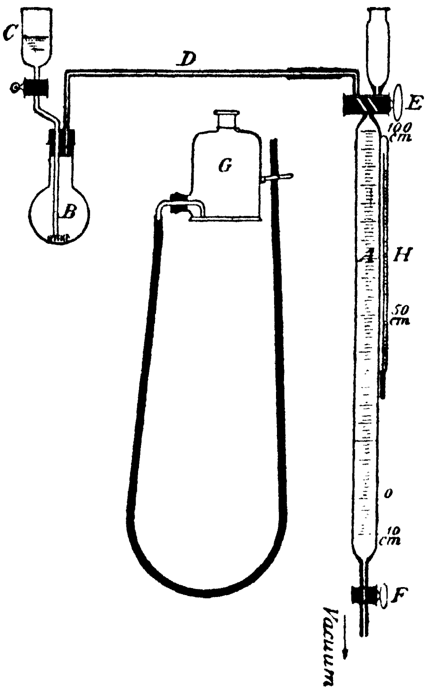

FIG. 215.

The substance in B is then decomposed by adding hydrochloric acid, drop by drop, from the tap-funnel C; when the evolution of gas slackens the contents of B are heated, and the complete evolution of the liberated gases is facilitated by the addition of from 2 to 3 c.c. of hydrogen peroxide; on again heating, the evolved oxygen drives out all the dissolved gas. The burette is then disconnected, allowed to stand for about twenty minutes and the volume of gas read, after adjusting the pressure by means of the bottle G. After taking the reading, a measured excess of an $N/10$ sodium arsenite solution is added, through the burette funnel, to absorb the chlorine, and any portion adhering to the funnel washed in with a little water; this solution floats on the heavier solution of brine. The carbon dioxide is then absorbed by sodium hydroxide solution introduced through E; as all the chlorine has been previously removed, no chlorate can be formed during this absorption. When the absorption is complete the residual volume of gas is read, which, deducted from the original reading, gives the volume of carbon dioxide and chlorine, after correcting each reading for temperature and pressure; the vapour pressure of the brine may be taken as 80 per cent. of that of pure water.

To determine the chlorine, the pressure-bottle is detached, and the contents of the burette are washed out into a beaker, acidulated with hydrochloric acid, an excess of sodium bicarbonate added, and the

unchanged arsenite titrated with $N/10$ iodine solution. The volume of carbon dioxide collected is then calculated by difference.

Bases.—As regards the bases, should only one be present, as is usual, the total quantity may be determined by conversion to sulphate by evaporating with sulphuric acid. Calcium and magnesium may also be determined as oxalate and pyrophosphate respectively, after first decomposing the hypochlorite by boiling with a strong acid.

Alkali Hydroxide and Carbonate.—Blattner[1] describes the following neat method for determining these constituents in Eau de Javel. It depends upon the fact that phenolphthalein preserves its red colour in hypochlorite solution so long as alkali hydroxide is present, but that the colour is destroyed by free chlorine as soon as all the hydroxide has been removed, and does not return on the further addition of free alkali. Ten c.c. of the bleach liquor is diluted with 150 c.c. of previously boiled distilled water, a few drops of a 1 per cent. alcoholic solution of phenolphthalein added, and the solution then titrated with normal acid, continuous agitation being maintained during the addition of the acid. The whole of the alkali hydroxide is neutralised when the coloration produced by the addition of a fresh drop of phenolphthalein solution disappears on shaking the solution for five seconds. Each 1 c.c. of normal acid used corresponds to 0·03100 g. Na_2O or 0·04001 g. NaOH. The total alkalinity, $NaOH + Na_2CO_3$, is determined in a second portion of the liquor by boiling with ammonia until the hypochlorite has been decomposed and all unchanged ammonia driven off, and then titrating with acid in the usual manner. The above methods are especially suitable for the examination of caustic potash or caustic soda solutions produced electrolytically, which usually contain hypochlorite.

The following is a very simple method of determining the free alkali. A small quantity of chemically pure, neutral hydrogen peroxide is added to the solution to decompose the hypochlorite, according to the equation $NaOCl + H_2O_2 = NaCl + O_2 + H_2O$, and the sodium hydroxide and carbonate present are then titrated in the usual manner (*cf.* p. 526). (In this connexion, see also Orton and Jones, p. 608.)

H. v. Huber[2] has described a method for the examination of electrolytic liquors which contain chromate. Phenolphthalein is, in this case, unsuitable as an indicator for the free alkali present; methyl orange, however, gives a perfectly sharp colour change at the point where potassium chromate is converted into the bichromate. If, therefore, the chromate content is known, it is only necessary to deduct from

[1] Lunge, *Sulphuric Acid and Alkali*, vol. iii., p. 601.

[2] *Z. Electrochem.*, 1901, 7, 396.

the total acid required for titration the quantity necessary to convert the chromate into bichromate. If the quantity of chromate present is not known, the chromate is precipitated by addition of barium chloride, and the solution then titrated with acid. Where the quantity of chromate present is small, it is not necessary to filter the solution before titrating. Any hypochlorite or free hypochlorous acid in the liquor must first be removed; this may be done without affecting the alkalinity, by addition of neutral sodium sulphite or of sodium thiosulphate. If sodium sulphite be used, an excess must be avoided, since with methyl orange the colour change only occurs when such excess has been converted to the acid sulphite which involves the consumption of the corresponding quantity of acid.

III. Potassium Chlorate

The potassium chlorate of commerce is usually almost chemically pure, and contains only a very small trace of chloride, the quantity of which should not exceed 0·05 per cent. For this reason it is necessary to take a somewhat large quantity of chlorate, say 50 g., for the determination of the *chloride*. The chlorate is dissolved in distilled water, and the chloride precipitated by addition of silver nitrate solution. The distilled water employed must be perfectly free from chlorides. The chlorate should dissolve without residue, and the solution should not be coloured by organic matter. Ammonium sulphide should not produce any coloration, indicating the absence of iron, manganese, or lead. Garnier[1] found arsenic in potassium chlorate.

Potassium Nitrate only occurs in potassium chlorate as an adulterant. It cannot be detected by fusing the chlorate and examining the melt for alkalinity, as pure potassium chlorate gives an alkaline reaction after fusion. The following reactions are most satisfactory.[2]

One g. of the salt is heated with 5 c.c. of sodium hydroxide solution; should ammonia be evolved, indicating the presence of ammonium salts, the solution is boiled until all ammonia has been expelled. The solution is then cooled, 0·5 g. of zinc filings and iron powder added, and the whole again heated. Any ammonia then liberated is due to the presence of nitrate. According to Scholvien,[3] the potassium chlorate is heated until the residual potassium chloride has also been brought to fusion. The melt is dissolved in water, and the solution treated with

[1] *Fischer's Jahresber.*, 1885, p. 260.
[2] Krauch, *The Testing of Chemical Reagents for Purity*, p. 244.
[3] *Apoth. Zeit.*, 1887, 408.

dilute sulphuric acid followed by zinc iodide and starch solution. The coloration produced should not be sufficient to render the solution opaque. A faint blue coloration is permissible, since with 0·01 per cent. of nitrate the colour produced is so intense that the solution is quite opaque.

A quantitative determination of the chloric acid in commercial chlorate is scarcely ever undertaken, owing to the small amount of impurity present; it may, however, be carried out as described on p. 598. This determination would be necessary for the indirect estimation of sodium and potassium chlorate in a mixture of the two salts; so far such mixtures do not, however, appear to occur in practice.

IV. Liquid Chlorine

The following physical properties of liquid chlorine are given by A. Lange.[1]

Specific gravity at 0°, 1·469; 15°, 1·426; 30°, 1·381.
Vapour pressure at 0°, 3·7; 15°, 5·8; 30°, 8·7 atmos.

One kilo corresponds to a volume of 316 litres measured at 0° and 760 mm. pressure.

Critical temperature, 146°.
Critical pressure, 93·5 atmos.
Boiling-point at 760 mm., $-33°·6$.
Melting-point of the solidified gas, $-102°$.

According to M. Pellaton,[2] the density of liquid chlorine is represented by the formula: $d=a+b(144-t)+c\sqrt{144-t}$, in which $a=0{\cdot}687014$, $b=0{\cdot}0002379$, and $c=0{\cdot}0622109$. He finds that the critical temperature is 144° and the critical pressure 76·1 atmospheres; and that the density of the saturated vapour can also be obtained from the above formula using $a=0{\cdot}48219$, $b=0{\cdot}002451$, $c=0{\cdot}068526$.

The chemical examination of the gas from the cylinders can be carried out by the methods for examining electrolytic chlorine (p. 591).

[1] *Taschenbuch. d. Berliner Bezirksvereines Deutscher Chemiker*, 1898-99, p. 82.
[2] *J. Chim. Phys.*, 1915, 13, 426.

[Table

Vapour Pressure and Specific Gravity of Liquid Chlorine.

R. Knietsch.[1]

Temperature.	Vapour Pressure.	Specific Gravity.	Mean Coefficient of Expansion.
−88° C.	37·5 mm. Hg.	...	...
85	45·0 ,,	...	...
80	62·5 ,,	1·6602	
75	88·0 ,,	1·6490	
70	118 ,,	1·6382	
65	159 ,,	1·6273	
60	210 ,,	1·6167	
55	275 ,,	1·6055	0·001409
50	350 ,,	1·5945	
45	445 ,,	1·5830	
40	560 ,,	1·5720	
35	705 ,,	1·5589	
33·6	760 ,,	1·5575	
30	1·20 Atm.	1·5485	
25	1·50 ,,	1·5358	
20	1·84 ,,	1·5230	
15	2·23 ,,	1·5100	0·001793
10	2·63 ,,	1·4965	
5	3·14 ,,	1·4830	
0	3·66 ,,	1·4690	
+ 5	4·25 ,,	1·4548	0·001978
10	4·95 ,,	1·4405	
15	5·75 ,,	1·4273	0·002030
20	6·62 ,,	1·4118	
25	7·63 ,,	1·3984	0·002190
30	8·75 ,,	1·3815	
35	9·95 ,,	1·3683	0·002260
40	11·50 ,,	1·3510	
50	14·70 ,,	1·3170	0·002690
60	18·60 ,,	1·2830	
70	23·00 ,,	1·2430	0·003460
80	28·40 ,,	1·2000	
90	34·50 ,,	...	...
100	41·70 ,,	...	...
110	50·80 ,,	...	...
120	60·40 ,,	...	...
130	71·60 ,,	...	...
146	93·50 ,,	Critical point.	...

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LUNGE, G.—*The Manufacture of Sulphuric Acid and Alkali*, vol. iii., 3rd edition, 1911.

LUNGE, G.—*The Technical Chemists' Handbook*, 1916.

[1] *Annalen*, 1890, **259**, 100.

CYANOGEN COMPOUNDS

By HERBERT E. WILLIAMS, Withington, Manchester

ONLY the technical methods of detection and estimation adopted in general practice and in the industry are described in the following section; the methods selected being those which combine speed with accuracy.

For details of the methods of preparation and manufacture, the physical and chemical properties of these compounds, and for alternative methods of estimation, the general chemical literature and special books on the subject should be consulted.

The general methods of estimation will be described first in detail, followed by an account of the special modifications required in applying the general method to particular commercial products.

It will be noticed that cyanide, ferrocyanide, ferricyanide, nitroferricyanide, and thiocyanate can each be estimated by a final titration with standard silver nitrate solution. Owing to the ease and accuracy with which the silver nitrate solution can be standardised, it will be found of advantage to adopt the methods based on the silver nitrate titration. These methods have the further advantage that they will be found simple, easy of manipulation, and accurate, and at the same time only one standard solution is necessary.

SIMPLE CYANIDES AND HYDROCYANIC ACID

Cyanides appear in the market mostly as the sodium or potassium salt, the former now rapidly supplanting the latter. A considerable quantity of hydrocyanic acid was manufactured for war purposes, but in normal times a comparatively small quantity of this compound, and of certain simple double cyanides which are used in medicine, etc., are produced on a manufacturing scale. Sodium cyanide is manufactured chiefly by the following processes:—

1. By passing dry ammonia through heated metallic sodium and then adding carbon.
2. By fusing anhydrous sodium or potassium ferrocyanide with metallic sodium.

3. By the recovery of hydrocyanic acid from the gases obtained in the dry distillation of beet residues in specially constructed furnaces.
4. By fusing calcium cyanamide with sodium chloride or carbonate and carbon.

Recently a process has been patented and a plant erected in America for the manufacture of sodium cyanide by passing nitrogen over a heated mixture of sodium carbonate, carbon, and finely divided iron, moulded into the form of briquettes, the finely divided iron acting as a catalyst. This process has yet to prove a serious competitor with the older processes mentioned above.

The chief use of sodium cyanide is for the extraction of gold from its ores; but of late years an increasing amount of cyanide is consumed in America as an insecticide in agriculture; the cyanide is converted into hydrocyanic acid where required.

Detection.—Hydrocyanic acid and the simple alkaline cyanides may be detected in solution by several well characterised reactions, the most important of which are:—

1. The solution is made alkaline with sodium or potassium hydroxide and the mixture warmed with a few drops of a solution of ferrous sulphate. The cyanide is converted into ferrocyanide, which may be recognised by slightly acidifying the mixture and adding dilute ferric chloride solution, when a deep blue precipitate of ferric ferrocyanide will be formed if a cyanide is present in the original solution.

If the solution is very dilute, it should first be made alkaline with a little sodium hydroxide—avoiding excess—and evaporated down to a small bulk before testing by the method described above.[1]

2. A small quantity of hydrocyanic acid or alkaline cyanide may be detected by acidifying the solution with tartaric acid and gently warming. The vapour which is evolved is allowed to act on a drop of ammonium sulphide (containing polysulphide) on a watch-glass. The drop is then evaporated carefully to dryness, taken up with a little water and a drop of a dilute solution of ferric chloride added; a red coloration shows the presence of a thiocyanate formed by the action of the hydrocyanic acid on the ammonium polysulphide. For this test ferrocyanides should be absent.

3. Cyanides in the solid state may be detected by gently fusing the solid with anhydrous sodium thiosulphate. By this means any cyanide present is converted into the thiocyanate, which may be detected by the red coloration produced on the addition of ferric chloride to the acidified solution of the fused salt. Ferrocyanides and the double cyanides generally will also give the above reaction.

[1] G. D. Lander and A. E. Walden, *Analyst*, 1911, 36, 266.

Hydrocyanic Acid

Hydrocyanic acid is too weak an acid to respond to an indicator, and therefore cannot be directly titrated with standard alkali solution. If, however, an excess of mercuric chloride solution is added, hydrochloric acid is liberated with formation of mercuric cyanide[1]:—

$$2HCN + HgCl_2 = 2HCl + Hg(CN)_2.$$

The liberated hydrochloric acid is readily titrated with standard alkali in the usual manner.

To a measured quantity of the solution containing not more than 1 per cent. of hydrocyanic acid, an excess of a neutral solution of mercuric and sodium chlorides—containing 27·1 g. $HgCl_2$ and 11·7 g. NaCl in 500 c.c. of water—is added. The solution is then titrated with $N/10$ alkali solution, using iodoeosin or other suitable indicator. Each c.c. of $N/10$ alkali = 0·0027 g. HCN (*cf.* p. 624).

Free hydrocyanic acid in the absence of other cyanides may be estimated by neutralising the acid with a slight excess of sodium hydroxide, adding a few drops of potassium iodide solution, and titrating the solution with $N/10$ silver nitrate solution until the first appearance of a permanent opalescence.

In the presence of an alkali cyanide, a portion of the solution is first titrated with silver nitrate solution with no other addition than a few drops of potassium iodide. A second and equal portion of the solution is neutralised with sodium hydroxide and then titrated with the silver solution after the addition of potassium iodide. The amount of silver solution required in the first titration is equivalent to the alkali cyanide present, and in the second to the alkali cyanide plus the hydrocyanic acid. Thus the difference of the second and first results gives the volume of alkali equivalent to the hydrocyanic acid. Each c.c. of $N/10$ silver nitrate = 0·0098 NaCN or 0·0054 HCN.

The *hydrocyanic acid in cherry laurel water and bitter almonds* is present partly in the free state, and partly in combination with benzaldehyde as a glucoside, and may be estimated by the following method[2]:—20 c.c. of a neutral solution of sodium sulphate (in which the benzaldehyde cyanhydrin is insoluble) is introduced into a separating funnel and 10 c.c. of the solution to be examined added, followed by 50 c.c. of ether and 10 drops of a 0·2 per cent. alcoholic solution of iodoeosine. The solution is then made just neutral, mercuric chloride solution is added, and the mixture well shaken. The aqueous solution is run off into a beaker containing distilled water, and the liquid

[1] L. Rosenthaler, *Arch. Pharm.*, 1910, **248**, 529; *J. Chem. Soc.*, 1910, **98**, 1119.
[2] L. Rosenthaler, *loc. cit.*

remaining in the separating funnel is washed with some sodium sulphate solution. The aqueous solution, which contains the hydrochloric acid equivalent of the free hydrocyanic acid, is then titrated with $N/10$ alkali.

The total hydrocyanic acid, both free and combined, may be estimated by adding a known excess of $N/10$ alkali hydroxide solution and a few drops of indicator to a measured quantity of the liquid. Mercuric chloride is then added, and the excess alkali titrated with $N/10$ sulphuric acid with vigorous shaking.

The total hydrocyanic acid in the solution taken is obtained by subtracting the number of c.c. of $N/10$ acid used from the volume of $N/10$ alkali originally taken, and multiplying the result by 0·0027.

Hydrocyanic Acid may be estimated in the presence of Cyanogen by the method proposed by F. Rhodes,[1] which depends on the fact that hydrocyanic acid reacts with silver nitrate in solution to precipitate silver cyanide, whereas with cyanogen no reaction takes place.

The gases containing the two compounds, or the vapours from the solution, are passed through two absorption flasks, the first containing 10 c.c. of a 10 per cent. solution of silver nitrate, acidified with a drop of dilute nitric acid, and the other 10 c.c. of $N/5$ potassium hydroxide solution.

In the first flask all the hydrocyanic acid is absorbed and precipitated as silver cyanide, which may be filtered, washed, and estimated. In the second flask the cyanogen is absorbed, and reacts with the alkali hydroxide to form equivalent amounts of cyanate and cyanide, thus:—

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O.$$

The cyanide may be estimated by washing out the contents of the absorption flask into a beaker and titrating the solution with $N/10$ silver nitrate. One c.c. of $N/10$ $AgNO_3$ = 0·0104 g. cyanogen.

Alkali Cyanides

The simple alkali cyanides are best determined by titrating with standard silver nitrate solution. This method, which is a modification of that first proposed by Liebig, is the one usually adopted in technical practice, as it has the advantages of speed and accuracy.

The gradual addition of a solution of silver nitrate to a solution of an alkali cyanide forms silver cyanide, which at first dissolves in the excess of alkali cyanide to form a soluble double salt, thus:—

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3.$$

A further addition of silver nitrate solution after this stage of the reaction has been reached produces a permanent opalescence due to the

[1] *J. Ind. Eng. Chem.*, 1912, 4, 652.

precipitation of silver cyanide in a finely divided state. The first appearance of this opalescence indicates the end-point of the reaction.

The method is carried out as follows:—A few drops of a solution of sodium or potassium hydroxide are added to a measured volume of the solution to be estimated (containing cyanide equivalent to 0·1 to 0·15 g. of HCN) to neutralise any free hydrocyanic acid, followed by a few drops of a 10 per cent. solution of potassium iodide. $N/10$ silver nitrate solution is then slowly run in from a burette, the liquid being agitated, until the solution shows a faint opalescence which remains permanent after agitation and standing a short time. The first appearance of this opalescence may be more readily observed if the liquid is viewed against a black background.

The silver solution may be added fairly rapidly at first, and then with greater care as the precipitate redissolves more and more slowly.

Sulphides and free ammonia must be absent from the solution, and excess of alkali hydroxide should be avoided. Haloid salts do not interfere with the reaction; in fact, the potassium iodide is added to render the end-point more distinct, and to prevent high readings due to the presence of certain salts such as ferrocyanides or of excess of alkali hydroxides.

The estimation of cyanides in the presence of hydrocyanic acid has been described under hydrocyanic acid (p. 623). For very dilute cyanide solution $N/100$ silver nitrate should be used. Each c.c. of the $N/10$ silver nitrate solution = 0·0054 g. HCN, 0·01302 g. KCN, or 0·0098 g. NaCN.

The *simple double cyanides* such as those of *zinc*, *cadmium*, *nickel*, *copper*, *mercury*, *silver*, *etc.*, are best estimated by distilling a weighed quantity or a measured volume of the solution with dilute sulphuric acid, to which some sodium chloride is added if copper, mercury, or silver is present. The evolved hydrocyanic acid is passed through a condenser into a solution of sodium hydroxide. When all the hydrocyanic acid is distilled off, the dilute cyanide solution in the absorption flask is poured into a beaker, and the condenser and flask washed out with distilled water. The cyanide solution is then titrated with $N/10$ silver solution in the manner described above.

The *double cyanides of zinc* may be estimated by direct titration with standard silver nitrate solution if sufficient sodium hydroxide is added.

The use of a standard solution of a mercury or nickel salt has been proposed in place of the standard solution of silver nitrate, but with no advantage.

Certain *cyanides*, such as, for example, mercuric cyanide, *which ionise but slightly* in aqueous solution, cannot be estimated by Liebig's volumetric method as no reaction takes place on addition of the standard silver solution. If the solution is made alkaline with sodium

or potassium hydroxide, and aluminium powder added slowly with agitation, the whole of the mercury is precipitated; the cyanide can then be titrated by Liebig's method in the filtered solution.[1]

The estimation of *cyanides in the presence of ferrocyanides* is best carried out by the method proposed by W. Feld. A measured volume of the solution containing the cyanide is placed in a distilling flask, an excess of a solution of magnesium chloride added, the whole diluted to 300 c.c. and distilled, the vapours being passed through a condenser into a solution of sodium hydroxide. The cyanide solution thus obtained is titrated with $N/10$ silver nitrate.

The magnesium chloride reacts with the alkali cyanide forming magnesium cyanide, which hydrolyses on boiling into magnesium hydroxide and hydrocyanic acid which distils off:

$$2H_2O + MgCl_2 + 2NaCN = Mg(OH)_2 + 2HCN + 2NaCl.$$

If *sulphides* are also present, hydrogen sulphide will be driven off with the hydrocyanic acid, owing to the hydrolysis of the magnesium sulphide, and condensed in the alkali hydroxide solution. An equivalent amount of lead nitrate is therefore substituted for the magnesium chloride. The sulphide is thus retained in the still as black lead sulphide.

A small quantity of alkali cyanide may be estimated by first converting it into ferrocyanide, by warming the solution with sufficient ferrous hydroxide and an alkali. A slight excess of a ferric salt is then added to the acidified solution, and the Prussian blue suspension formed matched against a freshly prepared standard made from a known quantity of potassium ferrocyanide.

If the cyanide solution is very dilute, it is acidified with hydrochloric acid and the liberated hydrocyanic acid extracted by shaking the solution with ether in a stoppered separating funnel. The ethereal solution is then shaken with dilute sodium hydroxide solution, and the resulting cyanide titrated with $N/100$ silver nitrate solution.

COMMERCIAL CYANIDE

The cyanide of commerce may contain certain other salts as impurities, the amount and nature of which depend largely on the method of manufacture. The chief impurities likely to be present are carbonate, hydroxide, chloride, sulphide, cyanate, and possibly cyanamide, ferrocyanide, formate, silicate, thiocyanate, etc.

Although practically all the cyanide consumed in the gold extraction industry at the present time is the sodium salt, it is still the general practice to calculate the percentage of cyanide on the basis of the

[1] V. Borelli, *Gazz. Chim. Ital.*, 1907, **37**, 429.

potassium salt; thus pure sodium cyanide would be sold as 132 per cent. KCN, and cyanide of, say, 100 per cent. KCN may contain a considerable percentage of impurities such as sodium carbonate, etc.

Ten g. of the sample is carefully weighed out, dissolved in distilled water, and diluted to 1000 c.c. The distilled water used should be well boiled and cooled to free it from dissolved carbon dioxide and other gases.

1. **Cyanide.** Twenty-five c.c. of the above solution is measured into a beaker flask of 200 to 250 c.c. capacity, diluted with cold carbon dioxide-free distilled water, a few drops of a 10 per cent. solution of potassium iodide added, and with $N/10$ silver nitrate solution run in until the first appearance of a slight but permanent opalescence. The presence of chlorides or thiocyanates does not interfere with this titration, but sulphides must be absent. In the presence of the latter the solution must be shaken with a little freshly precipitated lead carbonate, filtered, and the precipitate thoroughly washed. The filtrate is then titrated in the manner described.

This method is both rapid and simple, and if carefully carried out is very accurate. The cyanide may if desired be estimated gravimetrically as silver cyanide, but this method is more tedious and has no advantages over the titration method. Moreover, chloride, thiocyanate, or other salts capable of forming a silver salt insoluble in nitric acid solution, will be precipitated with the silver cyanide. The precipitate is purified after washing by boiling it with mercuric acetate, when the silver cyanide is converted into mercuric cyanide and silver acetate. The silver in the filtered solution—which is equivalent to the cyanide originally present—may then be estimated by precipitating and weighing as silver chloride.

2. **Chloride.** For this estimation the whole of the cyanide must first be removed. One hundred c.c. of the cyanide solution is placed in a distilling flask, acidified with a slight excess of acetic acid, and distilled gently through a condenser into sodium hydroxide solution. When the distillation is complete, the liquid is washed out of the distilling flask, neutralised with a slight excess of ammonia, and evaporated to dryness on the water-bath or till free of ammonia. The residue is dissolved in distilled water, a few drops of potassium chromate solution added, and the solution titrated with $N/10$ silver nitrate, using potassium chromate as indicator. One c.c. of $N/10$ $AgNO_3 = 0.003546$ g. Cl or 0.005846 g. NaCl.

In the known absence of cyanate or thiocyanate, the following rapid method may be adopted. To 50 or 100 c.c. of the cyanide solution is added a slight excess of chloride-free zinc sulphate solution. The cyanide, carbonate, hydroxide, sulphide, and ferrocyanide will then be precipitated as insoluble zinc salt. The mixture is diluted to a definite

volume. Filter off an aliquot part, and titrate with $N/10$ $AgNO_3$ as above.

Another method due to K. Polstorff and H. Meyer[1] depends on the formation of a compound of hydrocyanic acid and formaldehyde which is not precipitated by silver nitrate. To the cyanide solution containing about 0·5 g. of the original sample is added a slight excess of sodium hydroxide, and then 20 to 30 drops of a 40 per cent. solution of formaldehyde (free from chloride). After standing a few minutes, 5 c.c. of strong nitric acid is added and the chloride titrated with $N/10$ silver nitrate.

3. **Carbonate.** To 100 c.c. of the cyanide solution is added an excess of barium nitrate or chloride solution, when the whole of the carbonate will be precipitated as barium carbonate. The precipitate is allowed to settle for an hour in the cold, out of contact with the air, then filtered and washed with recently boiled distilled water. The insoluble carbonate is transferred to the beaker in which it was precipitated, distilled water and a few drops of methyl orange solution added, and the whole titrated with standard $N/10$ nitric or hydrochloric acid.

One c.c. of $N/10$ acid $= 0·0053$ g. Na_2CO_3 or 0·00691 g. K_2CO_3.

4. **Alkali Hydroxide.** The alkali hydroxide, together with the carbonate, may be estimated in the following manner:—100 c.c. of the solution of the sample is diluted to 200 c.c. with freshly boiled distilled water, and a known volume of $N/10$ sulphuric acid added, sufficient to neutralise both the carbonate and hydroxide present, and to liberate a little hydrocyanic acid from the cyanide.

The hydrocyanic acid liberated corresponds to the excess of standard acid over that required to neutralise the hydroxide and carbonate. It is converted into an equivalent quantity of hydrochloric acid by the addition of an excess of mercuric chloride, and the free acid then titrated with $N/10$ alkali, using methyl orange as indicator. The excess of acid thus found, deducted from the total acid originally added, gives the amount of acid required to neutralise the hydroxide and carbonate together. From this figure is then deducted the acid equivalent to the carbonate present, as determined by the method described above. The remainder multiplied by 0·004 will give the weight of hydroxide in the cyanide taken, calculated as sodium hydroxide.

The hydroxide may also be estimated by a modification of the method described by Clenell.[2] To 100 c.c. of the cyanide solution standard silver nitrate solution is gradually added until a faint but permanent opalescence appears; an excess of barium nitrate is then added to precipitate the carbonate, the solution filtered and washed with carbon dioxide-free distilled water. The filtrate is then titrated

[1] *Z. anal. Chem.*, 1912, 51, 601.
[2] *Chem. News*, 1895, 71, 93. *Chemistry of Cyanide Solutions*, p. 63.

with decinormal acid, using phenolphthalein as indicator. One c.c. of $N/10$ acid = 0·004 sodium hydroxide.

Accurate results are said to be obtained by titrating the cyanide solution containing the hydroxide with Prussian blue suspension.[1] A measured volume of the cyanide solution is titrated with $N/10$ silver solution to faint opalescence, and barium nitrate solution added to precipitate the carbonate. The resulting solution after filtration is warmed to 30° or 40° C. and titrated with standard Prussian blue suspension until a faint blue colour remains permanent. The suspension is of course well shaken before use. The Prussian blue suspension is prepared by adding ferric chloride to a large excess of potassium ferrocyanide, washing the precipitate by decantation as much as possible, diluting to a definite volume and standardising against a solution of sodium hydroxide of known strength.

This method is very similar to the one described above, the Prussian blue suspension being substituted for the standard acid. It has no apparent advantage, and undoubtedly requires more care and preparation with an accuracy somewhat problematical.

5. **Cyanates.** The estimation of cyanates is based on the decomposition which these salts undergo when boiled in aqueous solution with a mineral acid, whereby ammonia and carbon dioxide are formed :—

$$HCNO + H_2O = NH_3 + CO_2.$$

To 100 c.c. of the cyanide solution dilute sulphuric or hydrochloric acid is added in slight excess and all the hydrocyanic acid has been boiled off in a draught chamber. The cyanide is evolved as hydrocyanic acid with the steam, while the cyanate is converted into ammonia and carbon dioxide, the former remaining in solution in combination with the mineral acid. When the reaction is complete, the solution is washed into a distilling flask, excess of sodium hydroxide solution added, and the ammonia distilled through a condenser into a measured excess of standard acid. The excess of acid is titrated with standard alkali. Each c.c. of acid neutralised by the ammonia = 0·0065 g. NaCNO or 0·0081 g. KCNO in the weight of sample taken.

6. **Sulphide.** An excess of freshly precipitated lead carbonate is added to 100 c.c. of the cyanide solution and the mixture thoroughly agitated. The lead sulphide and the excess of lead carbonate are filtered off, washed thoroughly, transferred from the filter paper to a small dish, and evaporated with an excess of nitric acid to oxidise the lead sulphide to sulphate. When the excess of nitric acid has been driven off, a little water is added, the precipitate filtered and thoroughly washed, and the lead sulphate weighed in the usual manner. Each g. $PbSO_4$ = 0·2575 g. Na_2S.

[1] A. Shland, Thorpe's *Dict. Appl. Chem.*, 1910, vol. i.

A modification of the above method has been proposed by T. Ewan.[1] A solution of 10 g. of the sample dissolved in a small quantity of water is titrated with a standard solution of lead nitrate, until a drop placed on a piece of filter paper produces no dark coloration with a drop of lead nitrate solution. The results obtained by this method are, however, too low, but for small quantities of sulphide results sufficiently accurate are said to be obtained by multiplying the results by 1·25, or by making a standard solution of 2·4 g. pure lead nitrate per litre and taking 1 c.c. as equivalent to 0·01 g. K_2S or 0·007 g. Na_2S.

E. C. Rossiter[2] proposed to determine the sulphide first by Ewan's method, and then to add to a fresh portion of the cyanide solution a weighed quantity of pure dry lead nitrate sufficient to precipitate all the sulphide plus 10 per cent. excess. The excess lead is then titrated with a solution of sodium sulphide previously standardised by iodine solution.

FERROCYANIDES

The ferrocyanides of commerce are met with chiefly in the form of the sodium, potassium, and ferric salts (Prussian blue). The alkali metal ferrocyanides are produced principally by extracting the complex iron and ammonia ferrocyanides from spent oxide of iron and cyanogen mud —products obtained in the purification of coal gas—and also by fusing alkali metal thiocyanates with metallic iron, dissolving the fused mass in water and crystallising the filtered solution. The various brands of Prussian blue are manufactured from sodium or potassium ferrocyanide, and the methods of analysis applicable to them are described in the section on "Paints and Pigments," Vol. II.

Detection.—The most characteristic test for a ferrocyanide is the blue precipitate or coloration produced when a ferric salt solution is added to a neutral or acid solution of a ferrocyanide. A cupric salt produces the equally characteristic chocolate brown precipitate of cupric ferrocyanide.

ALKALI FERROCYANIDES

The various methods for the determination of ferrocyanides may be roughly divided into the following classes:—

1. Estimation of the iron of the ferrocyanide.
2. The oxidation of the ferrocyanide to ferricyanide.
3. Titration of the ferrocyanide with a standard solution of a metallic salt.
4. Decomposition of the ferrocyanide into hydrocyanic acid.

Estimation of the Ferrocyanogen Iron.—In this method the iron of

[1] *J. Soc. Chem. Ind.*, 1909, 28, 10. [2] *J. Soc. Chem. Ind.*, 1911, 30, 583.

the ferrocyanide is converted into ferric sulphate either by igniting with strong sulphuric acid until the ferrocyanide is completely decomposed, or by boiling the solution of the ferrocyanide with an excess of ammonium or potassium persulphate, the iron being then estimated in the usual manner. This method is only applicable to ferrocyanides free from any other iron compounds and from organic matter, and is not to be recommended. Very serious errors have been made in the past by the use of this method in the analysis of the ferrocyanogen contents of spent oxide, etc.

Estimation by Oxidation with N/10 *Permanganate Solution.*—This method depends on the oxidation of the ferrocyanide to ferricyanide. The solution, containing not more than one g. of the ferrocyanide, is placed in a large porcelain basin of about 1000 c.c. capacity, acidified with dilute sulphuric acid (1 : 4), diluted to 600 to 700 c.c., and the permanganate solution slowly added from a burette with constant stirring. The end-point of the reaction is observed by the colour of the solution changing to a yellowish red.

The reaction which takes place may be expressed thus:—

$$5K_4Fe''(CN)_6 + KMnO_4 + 4H_2SO_4 = 5K_3Fe'''(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

The permanganate solution may be standardised by pure recrystallised potassium ferrocyanide $K_4Fe(CN)_6 3H_2O$, or better, by the dry calcium potassium ferrocyanide $CaK_2Fe(CN)_6$. This double salt is readily prepared by adding a solution of pure calcium chloride to a solution of potassium ferrocyanide, filtering, washing the crystalline precipitate, and drying it at 100° C. This salt has the advantage that it is easily prepared in the pure state and is anhydrous. A weighed quantity of this salt is decomposed by warming with a solution of sodium or potassium carbonate. After thoroughly washing the precipitate the filtrate is titrated with the permanganate solution.

This method has been modified by E. Muller and O. Diefenthaler,[1] and by H. Bollenbach.[2] The latter investigator suggests the addition of an excess of the permanganate solution to a distinct red-violet colour. A few drops of ferric sulphate solution are added, and the excess permanganate titrated with *N*/10 potassium ferrocyanide. A green precipitate is formed as each drop of the ferrocyanide solution enters the liquid, but disappears on stirring as long as the permanganate is in excess. The appearance of a uniform green tint therefore denotes the end of the reaction, and the amount of ferrocyanide originally present is obtained by deducting the number of c.c. of standard ferrocyanide used from the total volume of permanganate solution originally added.

Each c.c. of *N*/10 $KMnO_4$ is equivalent to 0·03684 g. $K_4Fe(CN)_6$ or 0·0212 g. $Fe(CN)_6$.

[1] *Z. anorg. Chem.*, 1910, **67**, 418.

[2] *Z. anal. Chem.*, 1908, **47**, 687.

This method is only applicable for the estimation of ferrocyanide solutions free from other oxidisable compounds; in the presence of these bodies the following procedure is usually adopted. A measured quantity of the ferrocyanide solution is diluted and acidified as described above, and an excess of permanganate solution added which not only converts the ferrocyanide to ferricyanide but oxidises all the oxidisable compounds present. The solution is then made alkaline, ferrous hydroxide added, and the solution warmed. The ferricyanide is reduced to ferrocyanide, but the other oxidised compounds are not reduced. The solution is then filtered, the precipitate thoroughly washed, and the filtrate, cooled if necessary, acidified with dilute sulphuric acid and titrated with $N/10$ permanganate in the manner described above.

This method is, however, open to the objection that the precipitate is very bulky and requires considerable washing, and also that if thiocyanate were originally present, hydrocyanic acid would be formed by the oxidation of this compound with permanganate. This acid, when the solution is subsequently made alkaline, would combine with the ferrous hydroxide to form more ferrocyanide, and thus give too high a reading in the final titration with permanganate.

In the author's experience this difficulty may be overcome, by substituting white manganese hydroxide for the ferrous compound. This modification has the further advantage that the addition of only a little manganese hydroxide is necessary, as the solution will contain a considerable proportion of manganese salt from the reduction of the permanganate in the first operation. The precipitate is far less bulky, is more easily washed, and no ferrocyanide can be formed from any hydrocyanic acid that may be liberated from thiocyanates in the preliminary oxidation.

This method and its modifications, though at times convenient, and applicable to solutions of comparatively pure ferrocyanides, is not to be recommended for general practice, and should not be used for the estimation of ferrocyanides in liquids obtained in the extraction of spent oxide or cyanogen mud.

Titration with a Metallic Salt Solution.—Either copper sulphate or zinc sulphate is used; other heavy metal salts have been proposed, but have not been generally adopted in practice and offer no advantage.

The precipitation of the ferrocyanides by standard copper sulphate solution, originally proposed by Bohlig, and subsequently modified by Knublauch,[1] was at one time the accepted standard method in the estimation of ferrocyanides, particularly in the valuation of spent oxide of iron, etc. As sulphides, thiosulphates, and thiocyanates interfere with the reaction, standard zinc sulphate was substituted for the copper salt.

[1] *J. Gasbeleucht.*, 1889, 35, 450.

This precipitant has the advantage that it is unaffected by sulphides, thiosulphates, or thiocyanates; and the composition of the precipitate obtained is more constant under slightly varying conditions than that of the copper salt. This method has been generally adopted in works practice. Of late years, however, the decomposition of the ferrocyanide into hydrocyanic acid, the absorption of this gas in sodium hydroxide, and the titration of the resulting cyanide with $N/10$ silver nitrate solution is the method generally used in standard practice.

a. Precipitation with Copper Sulphate.—The standard solution is prepared by dissolving 12·5 g. of pure recrystallised copper sulphate in 1000 c.c. of water and a few drops of sulphuric acid are added.

The solution is then carefully standardised, as described below, against a solution of pure ferrocyanide of known strength, and the copper sulphate solution strengthened or diluted until 1 c.c. will exactly precipitate ferrocyanide equivalent to 0·01 g. of ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$.

The ferrocyanide used for standardising the solution is usually pure dry recrystallised potassium ferrocyanide, or dry anhydrous calcium potassium ferrocyanide, $CaK_2Fe(CN)_6$, prepared as described above; the sodium salt should not be used.

Exactly 1·153 g. calcium potassium ferrocyanide is weighed out (= 1 g. $Fe_4[Fe(CN)_6]_3$), transferred to a beaker, a small quantity of distilled water and a slight excess of potassium carbonate solution being added. After heating to boiling, the precipitated calcium carbonated is filtered off and washed, and the filtrate diluted to 100 c.c. Twenty c.c. of this standard ferrocyanide solution is then measured into a precipitation beaker of 150 c.c. to 200 c.c. capacity, acidified with 25 c.c. of $N/5$ sulphuric acid, and 20 *c.c. of a saturated solution of potassium chloride added;* the latter addition, for reasons to be subsequently explained, is necessary, and must on no account be omitted.

Standard copper sulphate solution is run slowly from a burette into the solution thus prepared. The beaker and its contents are agitated by giving the beaker a rotary motion with the hand.

The end-point of the reaction is determined by dipping a strip of filter paper or drop reaction paper, about 1½ inches long and ¾ inches wide, into the liquid, so that about one-third of the strip is submerged. The strip is then removed from the liquid, held in the hand for a short time to allow the clear liquid to rise above the brown precipitate of copper ferrocyanide. The belt of the paper wetted by the clear solution is then touched with a glass rod which has been dipped into a 5 per cent. ferric chloride or iron alum solution, taking care that the iron solution does not spread on to the copper ferrocyanide precipitate. The formation of a blue colour at the junction of the two liquids indicates the presence of ferrocyanides still in solution, and more copper

solution must be added. The amount of blue colour formed in each test should be noted, and as it becomes less smaller quantities of copper solution should be added after each test.

It is advisable in the first titration to add 0·5 c.c. copper solution at a time towards the end of the titration, when a result will be obtained within this limit. In the second titration the copper solution is added slowly, keeping the liquid agitated, until the amount run in is that at which the blue was last seen in the first titration; and then added a drop at a time between each test until no blue coloration develops on the test paper after at least one minute.

A sample of ferrocyanide is estimated as in the standard method given above. Sulphides, thiocyanates, or any compound capable of forming an insoluble copper compound other than ferrocyanide, must of course be absent. The ferrocyanide is usually freed from these impurities by precipitating the acidified solution with a ferric salt, filtering, washing the blue precipitate, and decomposing it with a 5 per cent. solution of potassium hydroxide.

In carrying out this method the following points must be strictly observed. About the same volume of liquid, and roughly the same amount of ferrocyanide as that used in the standard titration, should be used in each test. An excess of potassium salts must be present in the solution to be titrated, and the addition of potassium chloride solution is made for this reason. In decomposing any insoluble ferrocyanide, potassium and not sodium hydroxide must be used.

Very considerable discrepancies in the results obtained by different workers have occurred in the use of this method through neglect of these conditions, but if the preceding directions are exactly followed, and with a little practice, this method is capable of yielding excellent results.

The composition of the copper ferrocyanide precipitate varies considerably when precipitated under different conditions. Thus the precipitate from potassium ferrocyanide contains more alkali metal, and therefore less copper for each ferrocyanogen equivalent, than when sodium ferrocyanide is used. Again, the amount of potassium in the precipitate varies up to a certain point with the quantity of potassium salts present. But in the presence of excess of potassium salt the composition of the ferrocyanide is constant, and therefore concordant results are obtained.

Sodium ferrocyanide and other soluble ferrocyanides except the ammonium salt may be estimated by this method, as they are converted into potassium ferrocyanide when an excess of potassium salts is added.

b. Precipitation by Zinc Sulphate Solution.—This method is identical in principle with the copper sulphate titration and differs but little in

detail. It has the important advantages that the presence of sulphides or thiocyanates does not interfere, and the presence or absence of the excess of alkali metal salts does not influence the amount of standard solution required to any great extent.

An investigation of this process has been made by F. W. Skirrow,[1] who states that in the titration of alkali metal ferrocyanides, the presence of alkali metal salts does not affect the result, but a longer time must be allowed in order to obtain a definite end-point. In the author's experience more accurate and concordant results are obtained by the use of excess of alkali metal salts, and this addition should be made.

The precipitate is not pure zinc ferrocyanide $Zn_2Fe(CN)_6$, but that obtained from potassium ferrocyanide is more or less pure potassium zinc ferrocyanide, $Zn_3K_2[Fe(CN)_6]_2$.

It is usual to work with a solution stronger than the standard copper solution given above, and 78 g. of pure crystallised zinc sulphate is dissolved in water with a few drops of sulphuric acid, and diluted to 1000 c.c. This solution is standardised against potassium ferrocyanide until 1 c.c. will precipitate ferrocyanide equivalent to 0·05 $Fe_4[Fe(CN)_6]_3$. Weaker solutions than the above may be used, but the solution must be standardised against a correspondingly smaller amount of the pure ferrocyanide.

The procedure is very much the same as that described for the copper titration. The solution containing the ferrocyanide is acidified with dilute sulphuric acid, an excess of a solution of potassium chloride added, and the solution titrated with the standard zinc sulphate solution; the end-point is observed by means of strips of filter paper, using dilute ferric chloride as indicator in the manner described above.

In the presence of thiocyanates, a longer time must be allowed for the blue colour to appear after the iron salt has been applied to the strip of filter paper. The blue colour will appear, if ferrocyanide is still present, at the outer edge of the red ferric thiocyanate coloration.

If much thiocyanate is present, the exact end-point is difficult to observe, and it is advisable first to precipitate the ferrocyanide as prussian blue with ferric chloride or iron alum solution, filter and wash, decompose by a solution of potassium hydroxide, dilute to a definite volume, and filter. A measured volume of the filtrate is then taken for titration.

Estimation as Hydrocyanic Acid.—The cyanogen contents of a ferrocyanide cannot wholly be converted into hydrocyanic acid by distilling the ferrocyanide solution with a dilute acid. From alkali

[1] *J. Soc. Chem. Ind.*, 1910, 29, 319.

metal ferrocyanides only about 50 per cent. can be obtained as hydrocyanic acid, the remainder being precipitated as ferrous alkali-metal ferrocyanide:—

$$2Na_4Fe(CN)_6 + 3H_2SO_4 = FeNa_2Fe(CN)_6 + 6HCN + 3Na_2SO_4.$$

The insoluble ferrous ferrocyanide may be slowly decomposed on boiling with a more concentrated acid, but it is impossible to adopt this reaction as a method of estimation; the time taken would be too long and some of the hydrocyanic acid would be decomposed by the strong mineral acid present with formation of ammonia and formic acid. Any oxidation of the ferrous ferrocyanide—which would be difficult to avoid—would result in the formation of the blue ferric compound which would remain undecomposed by the acid.

The difficulty of the complete decomposition of ferrocyanides into hydrocyanic acid has been overcome in the two methods described in detail below.

Distillation with acid in the presence of Cuprous Chloride.—This method, which has been worked out by H. E. Williams,[1] is based on the catalytic action of cuprous chloride. A small quantity of this salt added to an acidified solution of a ferrocyanide forms cuprous cyanide on boiling. This compound is then readily decomposed by the acid into hydrocyanic acid with regeneration of the cuprous chloride which attacks a further quantity of ferrocyanide. These reactions take place alternately until all the ferrocyanide has been decomposed and the hydrocyanic acid driven off with the steam.

A volume of the solution containing about 0·5 g. of the ferrocyanide is measured into a distilling flask of about 350 to 400 c.c. capacity, and diluted to 100 to 150 c.c. with distilled water. 0·1 g. of cuprous chloride is weighed out, washed with a little dilute sulphuric acid to remove any basic cupric chloride that may be present, the residue dissolved in a few cubic centimetres of a saturated solution of sodium or potassium chloride, and added to the ferrocyanide solution in the distilling flask. The flask is then agitated gently, 50 c.c. of $4N$ sulphuric acid is added, and the mixture distilled. The flask is connected to a condenser, to which are attached two absorption flasks containing a dilute solution of sodium hydroxide.

After distilling for a short time, the white precipitate which is at first formed changes to light blue and then gradually disappears, leaving the solution clear. When this stage is reached, the distillation should be continued for a short time longer to drive off the last traces of hydrocyanic acid. The absorption flasks are then disconnected, thoroughly washed out into a titration beaker, a few drops of a 10 per cent. solution of potassium iodide added, and the solution titrated

[1] *J. Soc. Chem. Ind.*, 1912, 31, 315.

with standard $N/10$ silver nitrate solution as described in the estimation of cyanides on p. 624.

$$1 \text{ c.c. of } N/10 \ AgNO_3 = 0.0070623 \text{ g. ferrocyanogen } Fe''''(CN)_6$$
$$\text{or } 0.009545 \text{ g. } Fe_4'''[Fe(CN)_6]_3 \text{ or } 0.01227 \text{ g. } K_4Fe(CN)_6.$$

This method may be applied to any of the soluble or sparingly soluble double salts of the alkali or alkaline earth ferrocyanides, also to the freshly precipitated insoluble ferrocyanides, such as those of zinc, cadmium, manganese, nickel, etc., but not to cupric ferrocyanide and the ferrocyanides of those metals which would oxidise the cuprous chloride or form stable double cyanides.

The preparation of a standard solution of cuprous chloride has been proposed by H. G. Coleman,[1] who recommends the use of a 10 per cent. solution of cuprous chloride in hydrochloric acid and the addition of some strips of copper to maintain the copper in the cuprous state.

Oxidising agents, sulphides, thiosulphates, and thiocyanates should be absent. The ferrocyanide is readily purified from these salts by precipitation with a ferric salt in acidified solution, filtering and washing the precipitated blue and decomposing it with a 5 per cent. solution of sodium hydroxide, again filtering and washing, and then adding the filtrate to the distilling flask.

This method of ferrocyanide estimation is both simple and accurate, and is rapidly replacing the heavy metal precipitation method in technical practice.[2]

Conversion into Mercuric Cyanide and Distillation with an Acid.[3]— In this method the ferrocyanide is first converted into mercuric cyanide and the latter body distilled with dilute acid. The evolved hydrocyanic acid is absorbed in alkali hydroxide solution and the cyanide formed titrated in the usual manner.

A measured quantity of the solution containing about 0·5 g. of the ferrocyanide is diluted to 150 c.c. with distilled water, 10 c.c. of $N/1$ sodium hydroxide solution added, and the mixture boiled to decompose any insoluble ferrocyanide that may possibly be present. After about ten minutes' boiling 15 c.c. of a 30 per cent. solution of pure magnesium chloride solution is added. This addition must be made gradually and with constant agitation to prevent the formation of clots of magnesium hydroxide and to obtain the precipitate in as fine a state of division as possible. This mixture is again boiled, then 100 c.c. of $N/10$ mercuric chloride is added and the boiling continued for a

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 323T.

[2] H. G. Coleman and E. W. Yoeman, *J. Soc. Chem. Ind.*, 1918, **37**, 322T; P. E. Spielmann and H. Wood, *ibid.*, 1919, **38**, 43T.

[3] W. Feld, *J. Gasbeleucht.*, 1903, **46**, 365; *J. Soc. Chem. Ind.*, 1903, **22**, 1068.

further fifteen minutes. The whole of the ferrocyanide is thus decomposed and the cyanogen remains combined with the mercury as mercuric cyanide.

The resulting mixture is placed in a distilling flask and 25 c.c. of $5N$ sulphuric acid added. The flask is fitted to a condenser which is connected to two absorption flasks containing dilute sodium hydroxide. The liquid is then gently distilled until the mercuric cyanide is decomposed and the whole of the hydrocyanic acid driven over into the absorption flasks. The absorption flasks are then disconnected, the liquid thoroughly washed out into a titration beaker and titrated with $N/10$ silver solution in the usual manner after adding a little potassium iodide solution.

This process has been studied by F. W. Skirrow,[1] who states that inaccurate results are obtained due to appreciable losses in the preliminary operation, but on the other hand H. G. Coleman[2] has found the process to yield theoretical results. In the author's experience accurate results may be obtained if the method is carried out exactly as described above, but that errors occur if the details of the method are not very carefully observed.

Examination of Commercial Ferrocyanides

The impurities likely to be met with in commercial salts are sulphur compounds, chiefly sulphates and thiocyanates from the mother liquor enclosed in the crystals.

In the precipitation of the ferrocyanide by the chloride of a heavy metal, the precipitate is so bulky and difficult to wash that only a small quantity of the ferrocyanide can be examined in this manner. The following method, however, will be found quite serviceable, the greater part of the ferrocyanide being first removed as a sparingly soluble crystalline double salt.

Ten g. of the sodium ferrocyanide is dissolved in 60 c.c. of water, a small excess of a strong solution containing magnesium and potassium chlorides in equivalent proportion added, and after boiling for one to two minutes, the crystalline potassium magnesium ferrocyanide filtered off. The filtration is rapid and the precipitate easy to wash. As the filtrate still contains a little ferrocyanide, a slight excess of zinc chloride is added and the precipitate filtered off and washed. This precipitate is comparatively small in amount and easily washed. In a measured portion of the filtrate the sulphate may be estimated by barium chloride in the well-known manner; and the thiocyanate in another portion either colorimetrically or by precipitation as the cuprous salt, which is thoroughly washed, decomposed by sodium hydroxide, and titrated with $N/10$ $AgNO_3$.

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 319.

[2] *Analyst*, 1910, **35**, 295.

In the examination of potassium ferrocyanide only magnesium chloride need be added to precipitate the double salt. With calcium ferrocyanide the bulk of the ferrocyanide may be removed by boiling with an excess of potassium chloride, the ferrocyanide separating as the sparingly soluble potassium calcium ferrocyanide. All reagents added must of course be free from sulphur compounds. In the examination of *prussian blue* combined ammonia should be looked for as well as the combined alkali metals, sodium and potassium. Many blues on the market to-day contain combined ammonia in place of the potassium of former times. For further details of the examination of prussian blue see the Section on "Paints and Pigments," Vol. II.

FERRICYANIDES

The ferricyanides are usually prepared by the oxidation of the ferrocyanides, and a number of oxidising agents have been proposed for this purpose. In the preparation of the potassium salt it is usual to pass chlorine through the solution of potassium ferrocyanide, and to separate the potassium ferricyanide by crystallisation from the potassium chloride formed by the reaction.

Detection.—A solution of ferrous sulphate added to a neutral or acid solution of a ferricyanide produces a deep blue precipitate (Turnbull's blue), thus distinguishing it from the ferrocyanide which gives only a bluish-white precipitate. With a solution of a ferric salt only a brown coloration is produced by a ferricyanide; if a small quantity of ferrocyanide is also present a green precipitate is formed.

Estimation of Ferricyanides.—These compounds are reduced to ferrocyanides and the latter estimated by any of the methods previously described. The reduction of the ferricyanide is best effected by making the solution alkaline and reducing the ferricyanide by the addition of certain metallic hydroxides, such as, for example, ferrous, manganous or cobaltous hydroxide. The reaction with ferrous hydroxide may be expressed thus:—

$$2K_3Fe(CN)_6 + 2Fe(OH)_2 + 2KOH = 2K_4Fe(CN)_6 + 2Fe(OH)_3.$$

A number of special methods have been proposed for the direct estimation of ferricyanides, but none of these possess any advantage over the general method given above.

A solution containing about 0·5 g. of ferricyanide is diluted, if necessary, with distilled water, made alkaline with sodium hydroxide, and an excess of ferrous or manganous hydroxide added. The solution is warmed to complete the reduction, filtered, and the precipitate thoroughly washed. The filtrate may then be titrated with standard zinc or copper sulphate solution, or put into a distilling flask, acidified

with an excess of dilute sulphuric acid, 0·1 g. cuprous chloride added, the mixture distilled, and the estimation completed as described for ferrocyanides on p. 636.

1 c.c. $N/10$ $AgNO_3$ = 0.01097 g. $K_3Fe(CN)_6$ or 0.007063 g. $Fe'''(CN)_6$.

Mixtures of Ferro- and Ferricyanides.—The reaction of a ferric salt cannot be used as a means of separating the two classes of compounds. In the presence of the two iron cyanogen compounds, the precipitated ferrocyanide contains a considerable proportion of the ferricyanide. If the ferricyanide is in large excess, a green precipitate of a ferric ferroferricyanide which contains both ferric ferrocyanide and ferric ferricyanide in a simple molecular proportion, is formed.

A convenient method[1] of separation which depends on the different reaction of the two zinc salts in the presence of an excess of sodium carbonate is described below. Sodium carbonate is added in excess to the solution containing about 1 g. of the mixed iron cyanogen compound. An excess of recently precipitated pure zinc carbonate is then added and the mixture warmed and agitated. The whole of the ferrocyanide is precipitated as a double zinc sodium ferrocyanide, while the ferricyanide remains in solution. The mixture is then filtered, and the precipitate thoroughly washed. The filtrate, which contains the whole of the ferricyanide, is reduced by the addition of one of the metallic hydroxides mentioned above, again filtered and washed, the filtrate neutralised with dilute sulphuric acid, distilled with cuprous chloride and sulphuric acid, and the cyanide titrated with $N/10$ silver solution as described on p. 624. The original precipitate, which contains the whole of the ferrocyanide as the insoluble zinc salt, together with the excess zinc carbonate, is added to a distillation flask, together with the paper, and the whole distilled with dilute acid and cuprous chloride.

If the original solution contains other salts likely to interfere with the subsequent reactions, the two iron cyanogen compounds are precipitated together by adding an excess of zinc sulphate or chloride to the *acidified* solution, which is then filtered and washed from the contaminating salts. The mixed precipitate is then digested in an excess of sodium carbonate solution. The ferricyanide of zinc is decomposed and passes into solution, while the ferrocyanide remains unattacked. The separation is then effected as described above.

One c.c. of $N/10$ $AgNO_3$ = 0·01097 g. $K_3Fe(CN)_6$ or 0·012277 g. $K_4Fe(CN)_6$ or 0·0070633 g. $Fe(CN)_6$.

The two salts may also be separated by the method of Browning and Palmer,[2] which is based on the fact that while a cadmium salt precipitates both compounds, a thorium salt precipitates only the ferrocyanide. The solution containing the two salts is acidified with

[1] H. E. Williams, *Cyanogen Compounds*, p. 380. [2] *Z. anorg. Chem.*, 1907, **54**, 315.

dilute hydrochloric or acetic acid and the ferrocyanide precipitated by the addition of a slight excess of thorium nitrate, and the ferricyanide in the filtrate precipitated by the addition of cadmium chloride.

If the solution of the two salts is free from other oxidisable matter or organic matter, the ferrocyanide may be estimated by a direct titration with standard permanganate solution. The resulting solution is then reduced by ferrous or manganous hydroxide, the precipitate filtered off and thoroughly washed, and the filtrate again titrated with permanganate solution. If the number of c.c. of permanganate solution used in the first operation are deducted from the number obtained in the second, the equivalent of the ferricyanide is obtained.

One c.c. of $N/10$ permanganate solution $= 0{\cdot}03683$ g. $K_4Fe(CN)_6$ or $0{\cdot}0329$ g. $K_3Fe(CN)_6$.

NITROFERRICYANIDES (NITROPRUSSIDES)

These salts are prepared by the action of nitric acid on ferro- or ferricyanides. The chief representative of these compounds is the sodium salt $Na_2Fe(CN)_5NO.2H_2O$ which crystallises well in fine ruby red crystals.

Detection.—The addition of an alkali sulphide to a solution containing a nitriferricyanide produces a deep violet coloration. This test is very characteristic and sensitive, but the coloration is evanescent. Heavy metals in solution, which produce dark coloured sulphides, must be removed or the coloration will be masked.

Estimation of Nitroferricyanides.—The most convenient method is to boil the solution with sodium hydroxide, when the whole of the cyanogen is converted into ferrocyanide according to the following equation:—

$$36Na_2Fe(CN)_5NO + 83NaOH$$
$$= 30Na_4Fe(CN)_6 + 3Fe_2O_3 + 35NaNO_2 + NH_3 + 40H_2O.$$

The ferrocyanide, which is formed quantitatively, is estimated by any of the methods described under the section dealing with ferrocyanides, pp. 630-638.

A volumetric process for the direct titration of nitroferricyanide has been described by Fonzes-Diacon and Carquet[1] as follows:—An excess of a solution of cadmium nitrate is added to a known volume of the nitroferricyanide solution, the precipitated cadmium nitroferricyanide filtered and thoroughly washed. The precipitate is then dissolved in an excess of ammonia and titrated with a standard solution of sodium sulphide. A slight excess of sodium sulphide, after all the cadmium has been precipitated, produces the characteristic violet colour with the soluble nitroferricyanide which indicates the end-point.

[1] *Bull. Soc. Chem.*, 1903 [3], **29**, 636; *J. Soc. Chem. Ind.*, 1903, **22**, 883.

THIOCYANATES

The thiocyanates may be prepared by several synthetic reactions, the most important of which is the process of Crowther, Rossiter, and Hood,[1] in which ammonia, carbon disulphide, and calcium hydroxide are heated under pressure in an autoclave, when the following reaction takes place:—

$$2NH_3 + 2CS_2 + 2Ca(OH)_2 = Ca(CNS)_2 + Ca(HS)_2 + 4H_2O.$$

The bulk of the thiocyanate of commerce is, however, recovered in the purification of coal gas. When the gas is passed through a solution of calcium or sodium polysulphide, the following reaction between the polysulphide and the hydrocyanic acid in the gas takes place:—

$$Na_2S_5 + 2HCN = 2NaCNS + H_2S + S_2.$$

This process had a number of disadvantages and was considerably improved upon in the method of P. E. Williams,[2] who passes the crude gas through specially constructed purifiers containing moist spent oxide of iron. The hydrogen sulphide and ammonia of the crude gas condense in the moisture on the surface of the spent oxide forming ammonium sulphide solution, which immediately dissolves sulphur and forms a layer of ammonium polysulphide solution on the surface of each particle of oxide. As the gas passes through the moist oxide the hydrocyanic acid is dissolved by the surface layer, and reacts with the polysulphide to form ammonium thiocyanate:—

$$(NH_4)_2S_5 + HCN + NH_3 = (NH_4)CNS + (NH_4)_2S_4.$$

The oxide is sprayed from time to time with water or weak liquid from a previous operation to remove the thiocyanate formed and to keep the oxide moist.

Detection.—The most characteristic test for a thiocyanate is the deep red coloration produced by the addition of a ferric salt to the neutral or acidified solution. In testing for very small traces, colourless ferric nitrate should be substituted for the chloride or sulphate. As mercuric chloride discharges the red colour, mercury salts must be absent when applying the test. The coloration does not take place in the presence of excess of oxalic acid, nor, unless acidified, when a highly basic ferric salt is used. In very dilute solutions the best method of applying the test is to acidify the solution, add the iron salt, and shake with a small quantity of ether. The ferric thiocyanate, which is more soluble in the ether than in the water, appears in the ethereal zone at the top of the liquid.

A second characteristic test is obtained by adding a solution of

[1] B. P. 17846, 22nd September 1893, and 21451, 1893. [2] B. P. 23604, 1909.

cupric chloride or sulphate to the solution to be tested, and then a reducing agent such as a solution of a sulphite, bisulphite, dilute sulphurous acid or sulphur dioxide. A very finely divided precipitate of white cuprous thiocyanate is produced in the presence of a thiocyanate.

General Methods of Estimation

The determination of a thiocyanate is usually carried out by titration with standard silver nitrate solution, but it may also be done by converting it into the copper salt and estimating the copper contents of the precipitate, or by treating with an oxidising agent and estimating the amount of oxidising agent used or the amount of sulphuric acid formed by the oxidation of the sulphur of the thiocyanogen radicle.

a. Titration with N/10 Silver Nitrate (*Volhard's Method*).—This method is based on the reaction of silver nitrate with a soluble thiocyanate in neutral or nitric acid solutions, whereby insoluble silver thiocyanate is precipitated. The end-point is determined by adding a few cubic centimetres of ferric alum, ferric sulphate, or better still, ferric nitrate solution to the liquid before titration. The silver solution is then run in until the red coloration of ferric thiocyanate just disappears owing to the precipitation of the thiocyanate by the silver salt.

A measured quantity of the solution containing about 0·25 g. thiocyanate is placed in a conical beaker of 300 c.c. capacity and diluted to 100-150 c.c. with distilled water. If alkaline, the solution is neutralised with dilute nitric acid (1 : 1), 10 c.c. added in excess, followed by 5 c.c. of a 10 per cent. solution of ferric nitrate. Decinormal silver nitrate solution is slowly run into the mixture from a burette until all the thiocyanate is just precipitated, this point being clearly indicated by the total disappearance of the red coloration of the ferric thiocyanate. The end-point is more sharply defined if the colourless ferric nitrate is used.

The titration should not be performed rapidly, but the silver solution added slowly and the precipitation beaker agitated by giving it a gentle rotatory motion with the hand. If the precipitation has taken place too rapidly, some of the thiocyanate solution is occluded in the clots of insoluble silver thiocyanate. On standing for a short time, with occasional stirring, any thiocyanate so occluded will diffuse out and colour the liquid with a reddish tinge. For this reason all titrations should be left at least five minutes after the first disappearance of the red coloration, and subsequently corrected if necessary by adding more silver solution.

All chlorides or other compounds capable of forming a silver salt insoluble in cold dilute nitric acid must be absent. In the presence of these impurities the thiocyanate is separated as the insoluble cuprous salt as described below, washed, decomposed by boiling with an excess of sodium hydroxide, again filtered and the precipitated cuprous hydroxide washed. The filtrate is then neutralised with diluted nitric acid and titrated as described.

$N/10$ mercuric nitrate may be substituted for $N/10$ silver nitrate solution, and the writer has found this method very convenient and accurate; and as the thiocyanate of mercury is precipitated in the crystalline form, the occlusion of soluble thiocyanate in the precipitate is avoided. Cyanides, chlorides, bromides, iodides, or any salt which forms a non-ionisable mercuric compound in nitric acid solution, must be absent. The solution is not, however, so conveniently standardised as the $N/10$ silver nitrate.

Separation as Cuprous Thiocyanate.—If the thiocyanate solution contains other salts capable of yielding a precipitate with silver insoluble in dilute nitric acid, it must be separated from them by precipitation as the cuprous salt. A solution containing not more than 1 g. thiocyanate is acidified by dilute sulphuric acid and sodium bisulphite added, followed by an excess of cupric sulphate. It is warmed to 40° to 50° and left to stand a short time. The precipitate is filtered and washed with water containing a small quantity of potassium sulphate in solution, to prevent the copper salt from passing through the paper in the colloidal form. When thoroughly washed, the precipitate, together with the filter-paper, is placed in the beaker in which it was precipitated and 100 c.c. of a 5 per cent. solution of sodium hydroxide (chlorine-free and purified by alcohol) added. The mixture is gently heated to boiling, and stirred to break up any clots of the cuprous thiocyanate. The solution is then cooled, filtered, and filtrate and washings made up to a definite volume. A portion of the solution containing about 0·25 g. thiocyanate is measured into a beaker, neutralised with dilute nitric acid, keeping the solution cool by running water if necessary, an excess of the dilute nitric acid and the iron salt indicator added, and the solution titrated with $N/10$ silver nitrate as above described.

In place of the acid and sodium bisulphite as a reducing agent for the cupric salt, sulphur dioxide gas may be bubbled through until the solution is saturated with it. Ferrous sulphate should not be used as a reducing agent, for the reaction

$$2CuSO_4 + 2FeSO_4 + 2NaCNS \rightleftharpoons 2CuCNS + Fe_2(SO_4)_3 + Na_2SO_4$$

is a reversible one and requires large excesses of ferrous and cupric sulphates before the reaction from left to right approaches completion.

Large excess of salts in solution gives rise to inaccuracies and should be avoided.

In the presence of ferrocyanides a preliminary precipitation with ferric or zinc sulphate is necessary, the thiocyanate being then precipitated by the copper and reducing agent in the filtrate from the insoluble ferrocyanide. Chlorides or bromides are removed in the filtrate from the copper thiocyanate, but iodides must be absent or the thiocyanate precipitate will be contaminated with cuprous iodide.

A method of estimating thiocyanates by adding a standard solution of cupric sulphate to the thiocyanate solution containing the reducing agent has been suggested. The end-point is noted by the formation of a brown coloration when a drop of the clear liquid is tested on a white tile with a drop of ferrocyanide solution. This end-point, however, is not sharp, and quite an appreciable excess of copper is required to produce a detectable colour by the drop reaction. The method is therefore not recommended for accurate work.

b. Oxidation by N/10 Permanganate.—This method depends on the oxidation of the sulphur of the thiocyanate to sulphuric acid, with liberation of hydrocyanic acid according to the following equation :—

$$5KCNS + 12H_2SO_4 + 6KMnO_4 = 11KHSO_4 + 6MnSO_4 + 5HCN + 4H_2O.$$

A solution containing 0·1 – 0·15 g. of the thiocyanate is placed in a large porcelain dish, considerably diluted, neutralised with dilute sulphuric acid if alkaline, and an excess of 50 c.c. of 10 per cent. acid added. Decinormal permanganate is then run slowly in from a burette, stirring the solution the while, until the first appearance of a faint pink tinge. One c.c. of $N/10$ permanganate solution $= 0{\cdot}001619$ g. KCNS or 0·000968 g. CNS.

For standardising the permanganate solution pure cadmium thiocyanate should be used. This salt is sparingly soluble, easily prepared, crystallises in well-defined crystals, and is anhydrous and non-deliquescent.

It has been shown by Grossmann and Hölter[1] that only about 95 per cent. of the thiocyanate is oxidised by the permanganate in accordance with the reaction expressed above; and Schroder[2] states that the time taken for the titration is an important point, and liable to give rise to variable results. To eliminate these errors as much as possible, the permanganate solution should be standardised against a pure thiocyanate and the same conditions of working adhered to in the subsequent titrations.

This method can only be applied to the titration of comparatively pure thiocyanate, which must of course be free from any other oxidisable matter. Insoluble thiocyanates may be estimated by first converting

[1] *Chem. Zeit.*, 1909, 33, 348. [2] *Z. öffentl. Chem.*, 15, 321-326.

them into a soluble thiocyanate by boiling with a dilute solution of sodium or potassium hydroxide.

In the presence of a metallic base soluble in the alkali hydroxide, such as zinc, ammonium sulphide is substituted for the hydroxide, and the filtrate from the insoluble sulphide evaporated to dryness on the water bath to remove the ammonium sulphide completely. The residue is redissolved in a little water, filtered if necessary, and estimated by $N/10$ silver nitrate solution. Estimation by permanganate is inadmissible if a sulphide has been used to remove the metallic base.

Estimation of traces of Thiocyanates.—The estimation of a very small quantity of a thiocyanate is usually carried out by matching the colour produced by adding an iron salt with that produced by a standard dilute thiocyanate solution treated in a similar manner (*cf.* p. 453).

The solution to be tested is put into a Nessler glass, acidified with dilute nitric acid, 2 c.c. of ferric nitrate solution added, and the whole diluted to a definite volume with distilled water. The colour is then matched by the method of guess and try with a standard solution of a thiocyanate, the same reagents being added and the solution diluted to the same bulk as the sample to be matched.

If the colour of the standard is too weak or too strong, more or less of the standard solution is taken and treated and compared in a similar manner, until the colour of the standard and the sample exactly match.

The following points must be observed in this method. The solution of the sample to be estimated should be free from colour, and ferric nitrate solution should be used as the iron salt. The same amount of iron salt and acid should be added in each case, as the reaction

$$Fe(NO_3)_3 + 3KCNS \rightleftharpoons Fe(CNS)_3 + 3KNO_3$$

is a balanced reaction, and the colour depends on the concentration of both iron and thiocyanate. Mercuric salts and oxalic acid prevent the reaction and should be absent.

For very small traces the estimation may be carried out by shaking the solution treated as above with ether in a stoppered graduated cylinder and matching the colour of the ethereal layer against a standard treated in a similar manner.

Commercial Thiocyanates

The chief thiocyanates of commerce are the aluminium, ammonium, barium, calcium, cuprous, potassium, and sodium salts. The impurities to be looked for in the soluble salts are chloride, sulphate, and thiourea, the latter more especially in the ammonium salt, particularly if it is made from thiocyanate gas liquor.

1. Sulphate and Chloride.—The sulphate is readily estimated by precipitation with barium chloride in the usual manner. The chloride,

however, cannot be directly estimated. The best method is to dissolve half a gram in 50 c.c. of distilled water in a tall straight-sided beaker, add 5 c.c. of nitric acid (sp. gr. 1·42) and gently heat to the boil. As the solution becomes warm, oxidation of sulphur takes place vigorously with evolution of hydrocyanic acid and nitrogen oxides. At times the action is violent and it is as well to cover the beaker with a watch-glass to prevent losses by spurting. The operation should be performed in a draught cupboard. When the oxidation is complete and the hydrocyanic acid driven off, excess of ammonia is added and the liquid evaporated to dryness in the water-bath. A little distilled water and a few drops of a 5 per cent. solution of potassium chromate are added and the chloride titrated with $N/10$ silver nitrate solution.

2. **Thiourea.**—The best method for the estimation of thiourea depends on the desulphiding action of silver nitrate in ammoniacal solution :—

$$(NH_2)_2CS + 2AgNO_3 + 2NH_4OH \rightarrow Ag_2S + 2NH_4NO_3 + H_2CN_2 + 2H_2O.$$

Unfortunately, a large excess of thiocyanate greatly interferes with the reaction, and it is necessary to remove the great bulk of the thiocyanate, before carrying out the test, by dissolving a weighed quantity of the salt in water and precipitating the bulk of the thiocyanate by a slight excess of lead acetate. The precipitate is filtered and washed. The excess lead in the filtrate is then removed by adding an excess of sodium carbonate and again filtering and washing the precipitate. This filtrate is then greatly diluted, made strongly ammoniacal, heated, and $N/10$ silver nitrate run into the hot solution drop by drop. Black silver sulphide is precipitated by the thiourea, and the addition of the silver solution is continued until no further precipitation of silver sulphide takes place. This point is quite readily observed as the silver sulphide clots in the hot alkaline solution and rapidly settles. One c.c. $N/10$ $AgNO_3$ = 0·0038 g. thiourea.

A small quantity of thiourea does not interfere with the titration of the thiocyanate by $N/10$ $AgNO_3$, but large quantities very seriously affect the results.

Cuprous thiocyanate finds a use as an antifouling composition for ships' bottoms, and should contain but a very small proportion of impurities. These will, of course, vary according to the method of manufacture and the impurities of the original thiocyanate solution used. Moisture, soluble salts, copper sulphide, free sulphur, and possibly organic matter should be looked for.

The *moisture* is estimated by heating a weighed quantity to 100° C. in a water-oven until the weight is constant. The heating has no influence on the cuprous thiocyanate, which is stable at a much higher temperature.

The *soluble salts*, which will usually consist of sodium chloride or sulphate, may be obtained by treating 10 g. of the salt with distilled water, boiling, filtering, and diluting the filtrate to a definite volume. Chloride and sulphate are determined in aliquot parts. Soluble thiocyanates and free acid should also be tested for.

The *insoluble impurities* may be obtained together by dissolving 5 or 10 g. of the salt in excess of a moderately strong solution of sodium or potassium thiocyanate when the cuprous thiocyanate will pass completely into solution. Any residue is filtered off through a weighed Gooch crucible containing a filter of asbestos, washed first with thiocyanate solution until free of cuprous thiocyanate and then with distilled water. The crucible is then dried to constant weight.

Any *free sulphur* present in the insoluble matter may be estimated by extracting the dried filter with carbon disulphide into a weighed flask. The solvent is then evaporated off, the flask heated in an oven to 100° C., dry air passed through to remove solvent vapour, and the flask cooled and weighed. *Copper sulphide* can be determined by boiling the residue with nitric acid, and the copper determined as cupric oxide in the filtrate, or if the amount is very small, by colorimetric methods. Impurities insoluble in acid may be determined by dissolving a weighed quantity of the salt in hot dilute nitric acid and weighing any residue. The presence of copper sulphide and organic matter degrades the colour of the salt, but sulphur is more harmful, as it is liable to oxidise to sulphuric acid.

The *thiocyanate* may be determined by decomposing a weighed quantity with an excess of a 5 per cent. solution of sodium hydroxide or carbonate, gently heating for some time and stirring with a glass rod to break up any lumps. After filtration the filtrate and washings are diluted to a definite volume and a portion titrated with $N/10$ silver nitrate solution. The results obtained by this method are liable to be low, for a number of reasons not yet fully elucidated, and the determination of the copper by any known method is more to be recommended.

CYANATES

The alkali metal cyanates are usually prepared from the corresponding cyanide, by oxidising the fused salt with a metallic oxide or oxidising agent, such as manganese dioxide, red lead, or potassium bichromate.

The cyanates of the alkali and alkaline earth metals are soluble in water, but those of the heavy metals are mostly insoluble and possess no characteristic colour.

Cyanic acid may be prepared in the anhydrous condition, but in aqueous solutions it rapidly decomposes. In concentrated solutions some cyanuric acid is formed by polymerisation of non-ionised cyanic

acid, but in dilute solution it takes up the elements of water, and rapidly and completely decomposes into ammonia and carbon dioxide.

Detection. The most characteristic test is the formation of the very sparingly soluble potassium cobalt cyanate. The solution is acidified with acetic acid and a solution of a cobalt and of a potassium salt added; the formation of small deep blue crystals indicate the presence of a cyanate.

In the presence of cyanides, carbon dioxide must first be passed through the liquid until all the cyanide is decomposed, and the potassium carbonate removed by filtering after the addition of 95 per cent. alcohol. The test described above is then applied to the filtrate.

Estimation of Cyanates.—The method proposed by Herting[1] is based on the decomposition of cyanic acid into carbon dioxide and ammonia :—

$$HCNO + H_2O = CO_2 + NH_3.$$

A measured quantity of the solution, containing 0·2 to 0·5 g. cyanate, is acidified with dilute sulphuric or hydrochloric acid, and the solution boiled for half an hour, when the reaction expressed by the above equation is complete. The solution is then transferred to a distilling flask, an excess of sodium hydroxide solution added, and the mixture distilled through a condenser into a measured volume of standard sulphuric acid.

The excess of acid is titrated with standard alkali, using methyl orange as indicator. Each cubic centimetre of $N/10$ acid neutralised by the liberated ammonia = 0·0081 g. KCNO or 0·0065 g. NaCNO.

The presence of cyanide does not interfere with the estimation, as the hydrocyanic acid is driven off on boiling the acid solution. Ferrocyanides or other iron cyanogen compounds, if present, should be removed by precipitating the solution, after acidification, with a ferric or ferrous salt (not iron alum) according to the particular iron cyanogen compound present. If ferrocyanides are present, the precipitate must be added to the alkaline solution in the distilling flask, before distilling off the ammonia, as when ferric ferrocyanide is precipitated in the presence of ammonium salts some of the ammonia combines with the precipitate.

The use of potassium hydrogen sulphate in place of the free mineral acid has been suggested by Wilbauer.[2]

Estimation by the Silver Salt.—This method depends on the fact that insoluble silver cyanate is decomposed by hot dilute nitric acid with the formation of silver and ammonium nitrates and carbon dioxide.

The solution to be estimated is precipitated with an excess of

[1] *Z. angew. Chem.*, 1901, **24**, 585.

[2] *Z. anal. Chem.*, 1903, **42**, 77.

silver nitrate solution, and the insoluble clotty precipitate of silver cyanate filtered, washed, and digested for about one hour with a measured quantity of standard nitric acid.

The silver cyanate is decomposed by this treatment according to the following equation:—

$$AgCNO + 2HNO_3 + H_2O = AgNO_3 + NH_4NO_3 + CO_2.$$

The amount of cyanate may then be determined in any of the following ways:—

1. Titration of the excess of standard nitric acid with standard alkali solution.
2. Titration of the silver nitrate produced, by standard $N/10$ potassium thiocyanate solution, using ferric nitrate as indicator, or by neutralising the excess of acid by ammonia, evaporating to drive off the free ammonia and titrating the resulting solution with $N/10$ sodium chloride, using potassium chromate as indicator.
3. Estimation of the ammonia formed, by distilling into standard acid, after adding an excess of sodium hydroxide as described above.

Chlorides, bromides, iodides, or cyanides do not interfere with this test, for although these salts form insoluble silver compounds, and are precipitated with the silver cyanate, they are not decomposed when treated with warm dilute nitric acid. Each cubic centimetre of $N/10$ HNO_3 consumed $=0{\cdot}00406$ g. KCNO, and each cubic centimetre $N/10$ KCNS or $N/10$ NaCl consumed $=0{\cdot}00811$ g. KCNO.

SPENT OXIDE OF IRON

Spent oxide of iron is produced in the purification of coal-gas. Hydrated bog-iron ore or artificially prepared hydrated iron oxide, mixed with peaty matter, sawdust, etc., to make a porous mass which the gas may readily permeate, is placed in layers in closed boxes called oxide purifiers, through which the foul coal-gas passes. The main reaction which takes place is the combination of the hydrogen sulphide of the crude gas with the iron oxide to form iron sulphides and water. When all the iron has been sulphided, the material is removed from the boxes and exposed to the air to revivify. The iron is thus re-oxidised with precipitation of free sulphur. When the revivification is complete the material is put back into the boxes and resulphided. In modern practice revivification is allowed to take place *in situ*.

The oxide may be used for purification until the percentage of sulphur in the mixture rises to about 45 to 50 per cent., when it is much

too inert to be of further use as a purifying agent, and is then replaced by fresh oxide.

Besides the main reaction mentioned above, a number of subsidiary reactions also take place between the purifying mixture and the minor impurities of the crude gas, thus:—

1. The hydrocyanic acid in the gas in conjunction with a little ammonia—which is always present—reacts with the iron sulphide to form ferrous ammonium ferrocyanide, which in contact with the air is converted into one or more of the ferric or ferrosoferric ammonium ferrocyanides.
2. The hydrocyanic acid in the presence of ammonium sulphide also reacts with the free sulphur to form ammonium thiocyanate.
3. In the revivification of the oxide a small portion of the sulphide is oxidised first to ferrous sulphate and finally to a basic ferric sulphate.
4. A considerable proportion of tarry matter is mechanically scrubbed out of the gas.

Thus the spent oxide is a somewhat complex mixture, containing not only the sulphur and the residue of the peat and sawdust mixed with the original oxide, but complex ferrocyanides, thiocyanates, sulphates, ammonia, pyridine, tar, etc.

The spent oxide is chiefly of value on account of the sulphur it contains for the manufacture of sulphuric acid, and is bought and sold on the percentage of free sulphur. When the ferrocyanide content is high enough (over $4\frac{1}{2}$ to 5 per cent.), the material is bought for the recovery of the ferrocyanides. Of late years, however, as the ferrocyanogen content of the spent oxide has gradually decreased for a number of causes—chiefly the growing use of the vertical retort—less of this material is available for ferrocyanide extraction.

It must be particularly emphasised that accurate methods of analysis are useless if the sampling is faulty. The sample, which should be a good average of the whole bulk, is very carefully ground, sifted, and well mixed, and no part of the sample rejected; any pieces of wood, sawdust, or fibrous material that cannot be made to pass through the sieve must be broken up as small as possible, mixed with the bulk, and on no account thrown away (see also p. 4).

A full analysis of the spent oxide is seldom required; only the moisture and sulphur, and sometimes the ferrocyanide, thiocyanate, and ammonia, are estimated.

1. Moisture.—Five g. of the finely-powdered spent oxide is weighed out into a small weighed porcelain dish and dried in the water oven at 100° C. to constant weight.

This figure, however, does not represent moisture only, but includes a small and variable proportion of naphthalene, light oils, and sometimes small quantities of ammonia, pyridine, or hydrocyanic acid. The figure obtained, therefore, is generally a little in excess of the actual moisture present. On the other hand, a small quantity of oxygen is absorbed by the oxide in the oxidation of some ferrous hydroxide or iron sulphides that have escaped the revivification process, and of some slight trace of free sulphur, the amount of which depends on the time of drying, which tend to counterbalance the above error.

2. **Ferrocyanides.**—The method in general use in the industry for the estimation of ferrocyanides in spent oxide is a modification of Knaublauch's method, the extracted and purified ferrocyanides being titrated with a standard solution of copper sulphate. Of late years zinc sulphate solution has been fairly generally substituted for the copper salt (see p. 634). At the present time Williams'[1] method of distilling the ferrocyanide with an acid and cuprous chloride into an alkaline hydroxide solution and titrating the cyanide produced is coming into general recognition as a simple and accurate method of estimation[2] (*cf.* p. 636).

Twenty-five g. of the finely ground spent oxide is digested at the ordinary temperature with 100 c.c. of a 10 per cent. solution of sodium hydroxide, with occasional stirring for eighteen to twenty hours; a convenient method is to pour the alkaline solution on to the spent oxide placed in a mortar and agitate with the pestle.

When the operation is completed the whole mixture—both soluble and insoluble—is poured into a graduated flask and diluted to 260 c.c., 10 c.c. being allowed for the bulk of the insoluble matter.

The mixture is thoroughly agitated and then filtered through a large-sized dry filter-paper. One hundred c.c. of the clear filtrate is acidified with dilute sulphuric acid (1 to 4) in a beaker of 250 c.c. capacity, and an excess of ferric sulphate or chloride added to precipitate the ferrocyanide as the blue ferric compound: the presence of excess of ferric salts is indicated by the red coloration due to the thiocyanate almost invariably present. The precipitated mixture is stirred, allowed to stand for about ten minutes to allow the precipitate to clot together, and then filtered through a large pleated filter-paper. The liquid is allowed to drain through, and the beaker and precipitate washed with boiling distilled water to which a little sodium sulphate has been added—to prevent the blue passing through the paper as a colloidal solution when washed—until the filtrate is free from colour. In this operation the ferrocyanide is freed from the thiocyanate and the bulk of the impurities.

[1] *J. Soc. Chem. Ind.*, 1912, **31**, 315.

[2] H. G. Coleman and E. W. Yoeman, *J. Soc. Chem. Ind.*, 1918, **37**, 322T; and P. E. Spielmann and H. Wood, *ibid.*, 1919, **38**, 43T.

When the "blue" is thoroughly washed it is removed from the funnel together with the filter-paper, placed in the beaker in which it was originally precipitated, 100 c.c. of 5 per cent. potassium hydroxide solution added, and the contents stirred with a glass rod until all the blue is decomposed. This operation is greatly assisted by the filter-paper, which readily breaks down to a pulp on stirring, and divides up the clots of "blue." When all the "blue" is decomposed it is washed without filtration into a graduated flask of 250 c.c. capacity, and diluted to the mark on the neck with distilled water, no allowance being made for the volume of the paper. The mixture is then thoroughly agitated and filtered through a dry paper.

The decomposition of the "blue" must not be hastened by heat, and the mixture must be diluted directly all the blue is decomposed and not allowed to stand in the strongly alkaline liquid. This prevents the free sulphur, which is frequently precipitated with the ferrocyanide, from passing into solution as polysulphide and thiosulphate, which would seriously interfere with the results obtained on subsequent titration with the copper solution. The filtrate prepared as above must be tested for the presence of sulphides, and if present they must be removed by agitation with lead carbonate and filtration.

Fifty c.c. of the final purified solution is measured into a precipitation beaker of 200 c.c. capacity, acidified with dilute sulphuric acid, 20 c.c. of potassium chloride solution added, and the liquid titrated with standard copper sulphate solution in the manner described on p. 633, observing all the precautions mentioned there.

If the copper solution is standardised so that 1 c.c. will precipitate the ferrocyanide equivalent to 0·01 g. ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, then as the solution taken corresponds to 2 g. spent oxide, the percentage of ferrocyanide in the spent oxide calculated as ferric ferrocyanide is readily obtained by dividing by two the number of cubic centimetres of copper solution required.

Titration with standard zinc sulphate solution in place of the copper salt offers some marked advantages, *e.g.*, the presence of sulphides in excess does not interfere. If a zinc solution of which 1 c.c. will precipitate ferrocyanides equivalent to 0·05 g. ferric ferrocyanide is used, 100 c.c. of the original alkaline extract (= 10 g. spent oxide) is taken, acidified and titrated with the zinc solution without separating the ferrocyanide by precipitation with an iron salt. The accuracy of the result thus obtained may be affected by two factors. If the thiocyanates are more than a trace, the end-point will be difficult to observe on account of the red colour of ferric thiocyanate; further, the organic matter in the original alkaline solution may hold small quantities of ferric hydroxide in colloidal solution. When the liquid is acidified this

iron hydroxide precipitates a small quantity of the ferrocyanide, which thus escapes estimation by the zinc.

It is better, therefore, for accurate work to precipitate the ferrocyanide, wash and decompose the blue as described above, and take 125 c.c. of the filtered and purified ferrocyanide solution for titration (= 5 g. spent oxide).

The results obtained by these titration methods are liable to be a little low, for reasons which there is not sufficient space to enter into here, but which are more fully dealt with elsewhere.[1]

Estimation as Hydrocyanic Acid. An aliquot part of the solution of the decomposed prussian blue, prepared as above described and equivalent to 1 or 2 g. of the spent oxide, is placed in a distilling flask, an excess of dilute sulphuric acid and 0·1 g. cuprous chloride dissolved in hydrochloric acid added, and the mixture distilled. The evolved hydrocyanic acid is passed through a condenser into a dilute solution of sodium hydroxide, and the resulting cyanide solution then titrated with $N/10$ silver nitrate as described on p. 624.

A simpler method of estimating the ferrocyanides in spent oxide, which is at the same time accurate and comparatively rapid, is a modification of the cuprous chloride method. The residue from the spent oxide, after extracting the sulphur by carbon disulphide, is carefully removed from the extraction apparatus, and after removing the excess carbon disulphide, boiled with water and filtered to extract the thiocyanates. The residue, together with the filter-paper, is boiled with 50 c.c. of a 5 per cent. solution of sodium hydroxide. The solution is then cooled, diluted slightly, filtered, and the insoluble matter washed. The filtrate and wash water are then distilled in the usual manner with cuprous chloride and acid, and the resulting cyanide titrated with silver solution.

3. **Thiocyanates.**—The thiocyanate in spent oxide may be estimated by treating 10 g. of the finely powdered spent oxide with distilled water, filtering and washing the oxide to 200 c.c. A measured volume of the solution is then titrated with $N/10$ silver nitrate. If chlorides are also present, they must be removed as described on p. 644.

4. **Ammonia.**—Five g. of the ground spent oxide is placed in a distilling flask, a slight excess of dilute sodium hydroxide added, and the mixture distilled into a measured volume of standard sulphuric acid. The excess of acid is titrated with standard alkali, using methyl orange as indicator. Very considerable frothing sometimes takes place in this estimation, but it may be overcome by substituting fresh calcium hydroxide for the sodium hydroxide.

5. **Sulphur.**—See p. 364 and "Illuminating Gas," Vol. IV.

[1] H. E. Williams, *J. Soc. Chem. Ind.*, 1912, 31, 315.

THIOCYANATE GAS LIQUOR

Thiocyanate gas liquor is produced by scrubbing the hydrocyanic acid from crude coal gas by means of polysulphide solution, or by allowing the gas to pass through layers of spent oxide[1] kept moist with a spray of water.

The finished solution contains about 20 per cent. of ammonium thiocyanate, some ammonium sulphide and carbonate, and small quantities of ammonium ferrocyanide, carbonylferrocyanide, thiosulphate, thiourea, tarry matter, and phenolic bodies.

It is used as a raw material for the manufacture of cyanides, and for the preparation of pure thiocyanate of ammonium and other bases. For the former purpose it is converted into the sodium salt, evaporated to dryness, fused with metallic iron, and redissolved in water. The ferrocyanide so produced is crystallised, dehydrated, and fused with metallic sodium for the production of sodium cyanide.

1. **Thiocyanates**.—Fifty c.c. of the liquor is diluted to 500 c.c. and thoroughly mixed; 50 c.c. of this solution is measured out, diluted with distilled water, a small quantity of iron alum added, and the mixture warmed to 60° C. to oxidise the small quantity of sulphide and thiosulphate present. If the colour of the iron alum solution completely disappears, more must be added, until the colour of the ferric thiocyanate persists. The mixture is then allowed to stand a short time to clot the precipitate of ferric ferrocyanide and carbonylferrocyanide, which is then filtered off. The precipitate is thoroughly washed with distilled water containing a small amount of sodium sulphate to prevent the "blue" from passing through the filter. The filtrate, which contains the whole of the thiocyanate, is then precipitated as the cuprous salt, filtered, washed, decomposed by chloride-free sodium hydroxide, again filtered and washed, and the filtrate diluted to 250 c.c. Fifty c.c. of this solution is then diluted, acidified with pure dilute nitric acid and titrated with $N/10$ $AgNO_3$, using ferric nitrate as indicator as described previously. The number of cubic centimetres of $N/10$ $AgNO_3$ required $\times 0{\cdot}0076 \times 100 =$ g. NH_4CNS per 100 c.c.

The washed precipitate of ferric ferrocyanide and carbonylferrocyanide may be decomposed by a dilute solution of sodium hydroxide, filtered and washed, and the filtrates distilled with cuprous chloride and sulphuric acid as described on p. 636. The resulting cyanide is titrated with $N/10$ silver nitrate. One c.c. $N/10$ $AgNO_3 = 0{\cdot}0094$ g. $(NH_4)_4Fe(CN)_6$.

If it is desired to separate any carbonylferrocyanide from the ferro-

[1] P. C. Williams, B. P. 23604 (1909).

cyanide, the alkaline solution resulting from the decomposition of the precipitated iron salts is first neutralised with dilute sulphuric acid, zinc sulphate solution added to precipitate the two iron cyanogen compounds, and the whole made alkaline with sodium carbonate. After agitation it is warmed to 40° C. for a few minutes and filtered. The filtrate, which contains the carbonylferrocyanide, and the insoluble ferrocyanide are separately distilled with sulphuric acid and cuprous chloride.

1 c.c. $N/10$ $AgNO_3$ = 0.0094 g. $(NH_4)_4Fe(CN)_6$ or 0.0107 g. $(NH_4)_3Fe(CN)_5CO$.

2. **Thiourea.**—The estimation of thiourea is carried out by the method described on p. 647. Fifty c.c. of the solution is precipitated with lead acetate in slight excess and filtered, and the precipitate of sparingly soluble lead thiocyanate washed. The lead in the filtrate is then removed by a slight excess of sodium sulphate and again filtered and the precipitate washed. The filtrate is then diluted to 200 to 250 c.c. with distilled water in a large flask, made strongly ammoniacal, and heated on the sand-bath. To the warm solution $N/10$ $AgNO_3$ is run in with agitation. One c.c. $N/10$ $AgNO_3$ = 0·0038 g. $(NH_2)_2CS$.

The titration of the thiocyanate by $N/10$ silver nitrate is very seriously interfered with by the presence of a considerable proportion of thiourea. Precipitation of the thiocyanate as the cuprous salt is useless as a method of separation, as the thiourea is also precipitated. If, however, the solution is acidified with dilute nitric acid and titrated with $N/10$ solution of mercuric nitrate, using ferric nitrate as indicator, a reading corresponding to the thiocyanate plus thiourea is obtained. A further and equal portion of the solution is then treated with lead acetate to remove the greater part of the thiocyanate as described above and the excess lead removed by sodium sulphate; the thiourea in the final filtrate may be determined by $N/10$ $AgNO_3$ as described above. The amount of thiourea so obtained is then deducted from the combined thiourea and thiocyanate reading of the $N/10$ mercuric nitrate and the remainder calculated as thiocyanate. One c.c. $N/10$ $Hg(NO_3)_2$ = 0·0076 g. NH_4CNS or 0·0076 g. $(NH_2)_2CS$, and as 1 c.c. of $N/10$ $AgNO_3$ = 0·0038 $(NH_2)_2CS$, half of the amount of silver nitrate consumed in the thiourea titration must be deducted from the $N/10$ $Hg(NO_3)_2$ reading, if equal volumes of the original solution were taken for each titration.

GAS LIQUOR.

This liquor contains ammonium sulphide and carbonate, together with small quantities of ammonium cyanide, thiocyanate, ferrocyanide, carbonylferrocyanide, thiosulphate, thiocarbonate, phenols, pyridine, etc.

Only the estimation of the cyanogen constituents will be considered here. The analysis of these liquors has been the subject of much investigation by Linder,[1] and the methods given below are based chiefly on his work.

It is necessary that the samples be analysed at the earliest possible moment and kept entirely out of contact with air, otherwise the ammonium sulphide will oxidise, forming thiosulphate and polysulphide, and the latter body will react with ammonium cyanide to form thiocyanate. Any ammonium thiocarbonate present in the liquor will, on standing, gradually decompose into ammonium thiocyanate and hydrogen sulphide.

1. **Thiocyanates.**—250 c.c. of the gas liquor is measured into a graduated flask, provided with a stopper fitted with connections for the supply of coal gas, 10 g. pure lead carbonate is added, the air displaced by coal gas, the stopper fixed and the flask well shaken, and left to settle. The clear liquor must be tested with a lead paper, and if sulphide is still present, more lead carbonate added. 150 c.c. of the clear supernatant liquid is boiled for 10 to 15 minutes to remove cyanide, cooled, and made up to 150 c.c. To 50 c.c. of this solution dilute sulphuric acid is added in slight excess, and the ferrocyanides precipitated by a very slight excess of iron alum solution. The precipitate is filtered off, and washed with a dilute solution of sodium sulphate to prevent the "blue" passing through the filter in a colloidal condition. This precipitate must be rejected, and cannot be taken for the estimation of the ferrocyanides owing to the fact that ammonium ferrocyanide is slightly decomposed in the preliminary boiling to remove cyanide, with evolution of ammonium cyanide.[2] In the absence of air this decomposition may be represented thus :—

$$2(NH_4)_4Fe(CN)_6 = Fe(NH_4)_2Fe(CN)_6 + 6NH_4CN.$$

Whereas in the presence of sufficient air the decomposition proceeds thus :[3]—

$$14(NH_4)_4Fe(CN)_6 + O_2 = 2Fe_2'''Fe''(NH_4)_8[Fe(CN)_6]_4 \\ + 36NH_4CN + 4NH_3 + 2H_2O.$$

To the filtrate from the ferric ferrocyanide a moderate excess of a solution of sodium metabisulphite is added, the liquid warmed to 60° to reduce any ferric salt present, and copper sulphate solution added in slight excess, as shown by the blue colour of the supernatant liquid. The mixture is then allowed to stand in a warm place for a short time to coagulate the precipitate, which is then filtered and washed, using a

[1] *Alkali Report*, 1903, pp. 31-39; 1909, pp. 15-19; and Appendix to *Alkali Report*, 1894-1917, pp. 17-27.

[2] H. G. Colman and E. W. Yoeman, *J. Soc. Chem. Ind.*, 1918, 37, 319T.

[3] H. E. Williams, *Chemistry of Cyanogen Compounds*, p. 95.

dilute solution of potassium sulphate as wash water. The insoluble cuprous thiocyanate is then washed out of the filter into the beaker in which it was originally precipitated, 25 c.c. of a 4 per cent. solution of sodium hydroxide added by pouring the alkali through the filter-paper to decompose and remove any thiocyanate left in the pores of the paper.

The solution is then warmed and stirred until the decomposition is complete, filtered, thoroughly washed with hot water, the filtrate cooled, acidified with dilute nitric acid in slight excess, and titrated with $N/10$ $AgNO_3$ solution, using a ferric salt as indicator.

In the absence of chlorides or compounds yielding an insoluble precipitate with silver nitrate in nitric acid solution, the liquor after treatment with lead carbonate, boiling off the cyanide and precipitation of the ferrocyanide, may be acidified with nitric acid and directly titrated with silver nitrate.

2. **Ferrocyanides.**—As the desulphided liquor cannot be boiled to remove the volatile ammonium cyanide before precipitation of the ferrocyanide owing to the loss of part of the cyanogen of the ammonium ferrocyanide, the following method is recommended by H. G. Colman.[1] To 100 c.c. of the sample a few drops of ammonium polysulphide are added in slight excess, and it is allowed to stand fifteen minutes to complete the conversion of the cyanide into thiocyanate. Lead carbonate is then added to remove the sulphide, and about 10 c.c. of $N/1$ sodium hydroxide added to convert the ferrocyanide into the sodium salt, which is stable during the boiling. The ammonia is then boiled off. The solution is acidified with dilute sulphuric acid and iron alum solution added in slight excess. The solution is then filtered and the precipitate washed with a dilute solution of sodium sulphate. The precipitate is then decomposed by washing the filter with $N/1$ sodium hydroxide and finally with water. The filtrate is then strongly acidified with sulphuric and distilled with a little cuprous chloride into $N/1$ sodium hydroxide. The cyanide so produced is titrated with $N/10$ silver nitrate.

Mayer and Hempel's method is as follows:—250 c.c. of the liquor is slightly acidified with sulphuric acid and the ferrocyanide precipitated by a slight excess of iron alum. The solution is then heated to 60° and the ferric ferrocyanide filtered off and washed. The cyanogen content of the precipitate is then determined by Feld's method for ferrocyanide estimation (p. 633).

3. **Cyanide.**—Feld's method:—An excess of a strong solution of lead nitrate is added to 50 c.c. of the liquor in a distilling flask and the mixture distilled into a solution of sodium hydroxide. The lead nitrate, which precipitates the sulphide, ferrocyanide, etc., reacts also with the ammonium cyanide forming lead cyanide, which decomposes

[1] *Loc. cit.*

on boiling into hydrocyanic acid and lead hydroxide. The evolved hydrocyanic acid is absorbed in the alkaline solution and the resulting cyanide titrated with $N/10$ silver nitrate. One c.c. $N/10$ $AgNO_3$ = 0·0088 g. NH_4CN.

This method is only applicable in the absence of free ammonia. In the presence of free ammonia the following procedure must be followed:—50 c.c. of clear liquor after removing the sulphide by shaking with lead carbonate is run into a slight excess of a 25 per cent. solution of aluminium chloride diluted to 200 c.c. The solution should then be acid to litmus paper; normal sodium carbonate solution is added until the solution is distinctly alkaline, followed by 10 c.c. of a 20 per cent. solution of lead nitrate, which should render the solution acid to litmus. The hydrocyanic acid is then distilled off and estimated as described above.

The cyanide may also be estimated in the filtrate after separation of the ferrocyanides obtained in Colman's method of ferrocyanide separation described above. This filtrate contains not only the thiocyanate originally present in the liquor, but also that formed by the action of the ammonium polysulphide in the cyanide. If the total thiocyanates are estimated, and the amount originally in the liquor as determined by the above method deducted, the thiocyanate equivalent of the cyanide is obtained.

CONCENTRATED AMMONIA LIQUOR

This liquid is prepared by preheating the ordinary ammonia gas liquor, when the greater bulk of the hydrogen sulphide and carbon dioxide is driven off, and then distilling the liquor, first to drive off the free ammonia and then with lime to decompose the fixed ammonium compounds. The distillate is condensed.

The liquid thus produced consists essentially of a solution of ammonia, containing small proportions of sulphide, carbonate, cyanide, thiocyanate, and ferrocyanide of ammonium.

The estimation of the cyanogen compounds in this liquor has been the subject of recent investigation by H. G. Colman and E. W. Yoeman,[1] P. E. Spielmann and H. Wood,[2] and E. Linder.[3]

Great care must be taken in sampling and in the preservation of the samples from the air to prevent subsidiary actions from taking place.

1. Cyanide.—In the method recommended by Colman and Yoeman,[4] 100 c.c. of the concentrated liquor is run from a pipette into a flask containing 100 to 200 c.c. of boiling water to which about 10 c.c. of $N/1$ sodium hydroxide has been previously added. The water must

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 319T.
[2] *Ibid.*, 1919, **38**, 43T.
[3] *Appendix to Alkali Report*, 1894-1917.
[4] *Loc. cit.*

be boiling for some minutes to remove all the dissolved oxygen before the addition of the liquor. When the bulk of the ammonia has been driven off by continued boiling, a solution of 5 g. lead nitrate is added and the mixture distilled for twenty to twenty-five minutes into a solution of 25 c.c. $N/1$ sodium hydroxide. When the distillation is complete, the sodium cyanide in the distillate is titrated with $N/10$ silver nitrate, using a few drops of potassium iodide solution as indicator. 1 c.c. $N/10$ $AgNO_3 = 0.00881$ g. NH_4CN.

E. Linder[1] has stated that this method is inaccurate in the presence of thiosulphates, due to the conversion of some of the cyanide into thiocyanate by boiling with the alkali in the presence of thiosulphate. He therefore suggests the following modification:— 250 c.c. of the liquor is run into a graduated flask, 10 g. lead carbonate added, and the whole shaken in the presence of coal gas: 200 c.c. of the clear supernatant liquor is boiled to remove the bulk of the ammonia after the addition of 50 c.c. of $N/1$ sodium hydroxide to fix the cyanide. The liquor is then cooled and diluted to 250 c.c.

One hundred c.c. of this solution is run into a slight excess of a 25 per cent. solution of aluminium chloride (say 10 c.c.) diluted to 150 c.c. The solution should now be acid to litmus paper: normal sodium carbonate is then added to remove the excess of aluminium chloride (3 to 4 c.c. should make the liquid alkaline to litmus), followed by 10 c.c. of a 20 per cent. solution of lead nitrate (solution acid to litmus) and the hydrocyanic acid distilled into $N/1$ sodium hydroxide. The resulting cyanide is then estimated by titration with $N/10$ silver nitrate in the usual manner.

2. **Thiocyanate.**—One hundred c.c. of the desulphided and ammonia-free solution prepared as above (=80 c.c. original) is slightly acidified with dilute sulphuric acid, a few drops of strong ammonia added, and the solution boiled for ten to fifteen minutes to expel all cyanide. A few drops of iron alum are added to the cooled solution in slight excess, the liquid filtered from the precipitated ferrocyanide, and the latter thoroughly washed. To the filtrate a moderate excess of a solution of sodium metabisulphite is added and the mixture heated to 60-70° to reduce the ferric salt. A distinct excess of a 10 per cent. solution of copper sulphate is added and the heating continued to incipient boiling.

The solution is filtered after standing a short time, and the precipitate thoroughly washed. The precipitate is then decomposed with 25 c.c. of a 4 per cent. solution of chloride-free sodium hydroxide and again filtered and washed. The cooled filtrate is acidified with dilute nitric acid, a few drops of a solution of ferric nitrate added, and then titrated with $N/10$ $AgNO_3$ in the usual manner. The prussian blue precipitate

[1] *Loc. cit.*

obtained in above should not be used for the estimation of the ferrocyanides.

3. **Total Cyanogen as Cyanide and Thiocyanate.**—A few drops of ammonium polysulphide are added to 100 c.c. of the untreated liquor till the solution shows a permanent excess of the polysulphide. Any cyanide present is thus converted into thiocyanate. After standing fifteen minutes to complete the reaction, the sulphide is removed by the addition of lead carbonate, and the filtrate boiled with the addition of about 10 c.c. $N/1$ sodium hydroxide till most of the ammonia is driven off. The solution is made slightly acid with dilute sulphuric acid, iron alum solution added in slight excess, and the precipitated ferrocyanide filtered off and thoroughly washed. The filtrate, which contains the whole of the thiocyanate originally present in the liquor, plus the thiocyanate equivalent of the cyanide, is precipitated as cuprous thiocyanate and estimated in the manner described above.

If the thiocyanate equivalent of the cyanide is deducted from the amount of thiocyanate found, the result will equal the amount of thiocyanate originally present in the liquor, or if the thiocyanate is known and deducted from the total figure the result will be the thiocyanate equivalent of the cyanide.

The cyanide and thiocyanate may be conveniently estimated colorimetrically by means of the tintometer, and this method has been developed by P. E. Spielmann and H. Wood.[1]

4. **Ferrocyanide.**—The ferrocyanide precipitate obtained above may be decomposed by dilute sodium hydroxide, and the precipitate washed and the ferrocyanide estimated by distilling the filtrate with dilute sulphuric acid and a little cuprous chloride as described on p. 636.

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[1] *J. Soc. Chem. Ind.*, 1919, **38**, 43T.

APPENDIX

NOTE.—*See p.* 681 *for complete Index of Tables in the Text*

TABLE I.

Table for correcting the Volume of Water or of Dilute Standard Solutions ($N/5$ or more dilute) to 15°.

This is a more convenient form, for practical work, of the Table on p. 33. If the temperature of the solution is $t°$, it is multiplied by the factor in column a, to correct the volume to 15°; or the value in column b is deducted from the observed volume.

$t°$.	*a.* Factor.	*b.* Value in c.c. to be deducted from each 100 c.c.	$t°$.	*a.* Factor.	*b.* Value in c.c. to be deducted from each 100 c.c.
15	1,0000	0	23	0,9986	0,135
16	0,9999	0,013	24	0,9984	0,156
17	0,9997	0,027	25	0,9982	0,179
18	0,9996	0,042	26	0,9980	0,202
19	0,9994	0,059	27	0,9977	0,227
20	0,9992	0,076	28	0,9975	0,252
21	0,9991	0,095	29	0,9972	0,278
22	0,9989	0,114	30	0,9970	0,305

TABLE II.

Table for reducing the Volume of a Gas to 0° C.

0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
1	0·996	0·993	0·989	0·986	0·982	0·978	0·975	0·972	0·968	0·965
2	1·993	1·985	1·978	1·971	1·964	1·957	1·950	1·943	1·936	1·929
3	2·989	2·978	2·967	2·957	2·946	2·936	2·925	2·915	2·904	2·894
4	3·985	3·971	3·956	3·942	3·928	3·914	3·900	3·886	3·872	3·859
5	4·982	4·964	4·946	4·928	4·910	4·893	4·875	4·858	4·841	4·824
6	5·978	5·956	5·935	5·913	5·892	5·871	5·850	5·830	5·809	5·788
7	6·974	6·949	6·924	6·899	6·874	6·850	6·825	6·801	6·777	6·753
8	7·970	7·942	7·913	7·885	7·856	7·828	7·800	7·773	7·745	7·718
9	8·967	8·934	8·902	8·870	8·838	8·807	8·775	8·744	8·713	8·682
10	9·963	9·927	9·891	9·856	9·820	9·785	9·750	9·716	9·681	9·647
11	10·96	10·92	10·88	10·84	10·80	10·76	10·73	10·69	10·65	10·61
12	11·96	11·91	11·87	11·83	11·78	11·74	11·70	11·66	11·62	11·57
13	12·95	12·91	12·86	12·81	12·76	12·72	12·68	12·63	12·59	12·54
14	13·95	13·90	13·85	13·80	13·75	13·70	13·65	13·60	13·55	13·50
15	14·95	14·89	14·84	14·78	14·73	14·68	14·63	14·57	14·52	14·47
16	15·94	15·88	15·83	15·77	15·71	15·66	15·60	15·55	15·49	15·43
17	16·94	16·87	16·82	16·75	16·69	16·64	16·58	16·52	16·46	16·40
18	17·93	17·87	17·81	17·74	17·67	17·61	17·55	17·49	17·43	17·36
19	18·93	18·86	18·79	18·72	18·65	18·59	18·53	18·46	18·39	18·83
20	19·93	19·85	19·78	19·71	19·64	19·57	19·50	19·43	19·36	19·29
21	20·93	20·84	20·77	20·69	20·62	20·55	20·48	20·40	20·33	20·26
22	21·92	21·84	21·76	21·68	21·60	21·53	21·45	21·37	21·30	21·22
23	22·92	22·83	22·75	22·66	22·58	22·51	22·43	22·35	22·26	22·18
24	23·92	23·82	23·74	23·65	23·56	23·48	23·40	23·32	23·23	23·15
25	24·91	24·81	24·73	24·64	24·55	24·46	24·38	24·29	24·20	24·11
26	25·91	25·81	25·72	25·62	25·53	25·44	25·35	25·26	25·17	25·08
27	26·90	26·80	26·71	26·61	26·52	26·42	26·33	26·23	26·13	26·04
28	27·90	27·79	27·69	27·59	27·50	27·40	27·30	27·20	27·10	27·01
29	28·90	28·78	28·68	28·58	28·48	28·38	28·28	28·17	28·07	27·97
30	29·89	29·78	29·67	29·57	29·46	29·36	29·25	29·15	29·04	28·94
31	30·89	30·77	30·66	30·55	30·44	30·34	30·23	30·12	30·01	29·91
32	31·88	31·76	31·65	31·54	31·42	31·32	31·20	31·09	30·98	30·87
33	32·88	32·76	32·64	32·52	32·40	32·30	32·18	32·06	31·94	31·84
34	33·88	33·75	33·63	33·51	33·38	33·27	33·15	33·03	32·91	32·80
35	34·87	34·74	34·62	34·50	34·37	34·25	34·13	34·01	33·88	33·77
36	35·87	35·74	35·61	35·48	35·35	35·23	35·10	34·98	34·85	34·73
37	36·87	36·73	36·60	36·47	36·33	36·21	36·08	35·95	35·82	35·70
38	37·86	37·72	37·59	37·45	37·32	37·19	37·05	36·92	36·79	36·66
39	38·86	38·71	38·58	38·44	38·30	38·16	38·03	37·89	37·75	37·62
40	39·85	39·71	39·56	39·42	39·28	39·14	39·00	38·86	38·72	38·59
41	40·85	40·70	40·55	40·41	40·26	40·12	39·98	39·83	39·69	39·55
42	41·85	41·69	41·54	41·39	41·24	41·10	40·95	40·80	40·66	40·52
43	42·84	42·68	42·53	42·38	42·22	42·08	41·93	41·78	41·62	41·48
44	43·84	43·68	43·52	43·37	43·20	43·05	42·90	42·75	42·59	42·45
45	44·84	44·67	44·51	44·35	44·19	44·03	43·88	43·72	43·56	43·41
46	45·83	45·66	45·50	45·34	45·17	45·01	44·85	44·69	44·53	44·38
47	46·83	46·65	46·48	46·32	46·15	45·99	45·83	45·66	45·50	45·34
48	47·83	47·65	47·48	47·31	47·13	46·97	46·80	46·63	46·47	46·31
49	48·82	48·64	48·47	48·29	48·12	47·95	47·78	47·60	47·44	47·27
50	49·82	49·64	49·46	49·28	49·10	48·93	48·75	48·58	48·41	48·24

Table for reducing the Volume of a Gas to 0° C.—*Continued.*

0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
51	50·82	50·63	50·45	50·26	50·08	49·91	49·73	49·55	49·38	49·21
52	51·81	51·62	51·44	51·25	51·06	50·89	50·70	50·52	50·35	50·17
53	52·81	52·62	52·43	52·24	52·05	51·87	51·68	51·49	51·31	51·13
54	53·81	53·61	53·42	53·22	53·03	52·84	52·65	52·46	52·28	52·10
55	54·80	54·60	54·41	54·21	54·01	53·82	53·63	53·44	53·25	53·06
56	55·80	55·60	55·40	55·19	54·99	54·80	54·60	54·41	54·22	54·03
57	56·80	56·59	56·39	56·18	55·97	55·78	55·58	55·38	55·19	54·99
58	57·79	57·58	57·37	57·16	56·95	56·76	56·55	56·35	56·15	55·96
59	58·79	58·57	58·37	58·15	57·93	57·74	57·53	57·32	57·12	56·92
60	59·78	59·56	59·35	59·13	58·92	58·71	58·50	58·30	58·09	57·88
61	60·78	60·56	60·34	60·12	59·90	59·69	59·48	59·27	59·06	58·85
62	61·78	61·55	61·33	61·10	60·88	60·67	60·45	60·24	60·03	59·81
63	62·77	62·54	62·32	62·09	61·86	61·65	61·43	61·21	60·99	60·77
64	63·77	63·53	63·31	63·07	62·84	62·63	62·40	62·18	61·96	61·74
65	64·76	64·53	64·30	64·06	63·83	63·61	63·38	63·15	62·93	62·70
66	65·76	65·52	65·29	65·04	64·81	64·58	64·35	64·13	63·89	63·67
67	66·75	66·51	66·27	66·03	65·79	65·56	65·33	65·10	64·86	64·63
68	67·75	67·50	67·26	67·02	66·77	66·54	66·30	66·07	65·83	65·60
69	68·75	68·50	68·25	68·01	67·75	67·52	67·28	67·04	66·80	66·56
70	69·74	69·49	69·24	68·99	68·74	68·50	68·25	68·01	67·77	67·53
71	70·74	70·48	70·23	69·98	69·72	69·48	69·23	68·98	68·74	68·49
72	71·74	71·48	71·22	70·96	70·70	70·46	70·20	69·95	69·71	69·46
73	72·73	72·47	72·21	71·95	71·69	71·44	71·18	70·93	70·67	70·42
74	73·73	73·46	73·20	72·93	72·66	72·41	72·15	71·90	71·64	71·39
75	74·72	74·45	74·19	73·92	73·65	73·39	73·13	72·87	72·61	72·35
76	75·72	75·45	75·18	74·90	74·63	74·37	74·10	73·84	73·58	73·32
77	76·72	76·44	76·17	75·89	75·61	75·35	75·08	74·81	74·55	74·28
78	77·71	77·43	77·15	76·87	76·59	76·33	76·05	75·78	75·51	75·25
79	78·71	78·42	78·14	77·86	77·58	77·31	77·03	76·75	76·48	76·21
80	79·70	79·42	79·13	78·85	78·56	78·28	78·00	77·73	77·45	77·18
81	80·70	80·41	80·12	79·83	79·54	79·26	78·98	78·70	78·42	78·14
82	81·69	81·40	81·11	80·82	80·52	80·24	79·95	79·67	79·39	79·11
83	82·69	82·39	82·10	81·81	81·51	81·22	80·93	80·64	80·36	80·07
84	83·69	83·39	83·09	82·79	82·49	82·20	81·90	81·61	81·32	81·04
85	84·68	84·38	84·08	83·78	83·47	83·17	82·88	82·58	82·29	82·00
86	85·68	85·37	85·07	84·76	84·45	84·15	83·85	83·55	83·26	82·97
87	86·68	86·37	86·06	85·75	85·43	85·13	84·83	84·53	84·23	83·93
88	87·67	87·36	87·05	86·73	86·42	86·11	85·80	85·50	85·20	84·90
89	88·67	88·35	88·04	87·72	87·40	87·09	86·78	86·47	86·16	85·86
90	89·67	89·34	89·02	88·70	88·38	88·07	87·75	87·44	87·13	86·82
91	90·66	90·34	90·01	89·69	89·36	89·05	88·73	88·41	88·10	87·79
92	91·66	91·33	91·00	90·67	90·34	90·03	89·70	89·38	89·07	88·75
93	92·66	92·32	91·99	91·66	91·33	91·01	90·58	90·36	90·03	89·72
94	93·65	93·31	92·98	92·64	92·31	91·98	91·65	91·33	91·00	90·68
95	94·65	94·31	93·97	93·63	93·29	92·96	92·63	92·30	91·97	91·65
96	95·65	95·30	94·96	94·61	94·27	93·94	93·60	93·27	92·94	92·61
97	96·64	96·29	95·95	95·60	95·25	94·92	94·58	94·24	93·91	93·57
98	97·64	97·28	96·93	96·58	96·24	95·90	95·55	95·21	94·87	94·54
99	98·64	98·27	97·92	97·57	97·22	96·87	96·53	96·18	95·84	95·50
100	99·63	99·27	98·91	98·56	98·20	97·85	97·50	97·16	96·81	96·47

Table for reducing the Volume of a Gas to 0° C.—*Continued.*

0°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°
1	0·961	0·958	0·955	0·951	0·948	0·945	0·941	0·938	0·935	0·932
2	1·923	1·916	1·909	1·903	1·896	1·889	1·883	1·876	1·869	1·864
3	2·884	2·874	2·864	2·854	2·844	2·834	2·824	2·815	2·805	2·795
4	3·845	3·832	3·818	3·805	3·792	3·779	3·766	3·753	3·740	3·727
5	4·807	4·790	4·773	4·757	4·740	4·724	4·707	4·691	4·675	4·659
6	5·768	5·747	5·728	5·708	5·688	5·668	5·648	5·629	5·609	5·591
7	6·729	6·705	6·682	6·659	6·636	6·613	6·590	6·567	6·544	6·523
8	7·690	7·663	7·637	7·610	7·584	7·558	7·531	7·506	7·479	7·454
9	8·652	8·621	8·591	8·562	8·532	8·502	8·472	8·444	8·414	8·386
10	9·613	9·579	9·546	9·513	9·480	9·447	9·414	9·382	9·349	9·318
11	10·57	10·53	10·50	10·46	10·43	10·39	10·35	10·32	10·28	10·25
12	11·53	11·49	11·45	11·42	11·38	11·33	11·30	11·26	11·21	11·18
13	12·49	12·45	12·41	12·36	12·32	12·28	12·24	12·20	12·15	12·11
14	13·45	13·41	13·36	13·31	13·27	13·22	13·17	13·13	13·08	13·04
15	14·42	14·37	14·32	14·27	14·22	14·17	14·12	14·07	14·02	13·97
16	15·38	15·32	15·27	15·22	15·17	15·11	15·06	15·01	14·96	14·91
17	16·34	16·28	16·23	16·17	16·12	16·06	16·00	15·95	15·89	15·84
18	17·30	17·24	17·18	17·12	17·06	17·00	16·94	16·89	16·82	16·76
19	18·26	18·20	18·14	18·07	18·01	17·95	17·89	17·83	17·76	17·70
20	19·23	19·16	19·09	19·03	18·96	18·89	18·83	18·76	18·69	18·64
21	20·19	20·12	20·04	19·98	19·91	19·84	19·77	19·70	19·62	19·57
22	21·15	21·08	21·00	20·93	20·86	20·78	20·71	20·64	20·56	20·50
23	22·11	22·03	21·95	21·88	21·80	21·73	21·65	21·58	21·50	21·43
24	23·07	22·99	22·91	22·83	22·75	22·67	22·59	22·51	22·43	22·37
25	24·03	23·95	23·86	23·78	23·70	23·61	23·54	23·45	23·37	23·30
26	25·00	24·91	24·81	24·73	24·65	24·56	24·48	24·39	24·30	24·23
27	25·96	25·87	25·77	25·69	25·60	25·50	25·42	25·33	25·23	25·16
28	26·92	26·82	26·72	26·64	26·54	26·45	26·36	26·25	26·17	26·09
29	27·88	27·78	27·68	27·59	27·49	27·39	27·30	27·20	27·10	27·02
30	28·84	28·74	28·64	28·54	28·44	28·34	28·24	28·15	28·05	27·95
31	29·80	29·70	29·59	29·49	29·39	29·28	29·18	29·09	28·99	28·87
32	30·76	30·66	30·55	30·44	30·34	30·23	30·12	30·03	29·92	29·81
33	31·72	31·61	31·50	31·39	31·28	31·17	31·06	30·97	30·86	30·74
34	32·68	32·57	32·46	32·34	32·23	32·12	32·01	31·90	31·79	31·68
35	33·65	33·53	33·41	33·30	33·18	33·06	32·95	32·84	32·73	32·61
36	34·61	34·49	34·37	34·25	34·13	34·01	33·89	33·78	33·66	33·54
37	35·57	35·45	35·32	35·20	35·08	34·95	34·83	34·72	34·59	34·47
38	36·53	36·40	36·28	36·15	36·02	35·90	35·77	35·66	35·53	35·40
39	37·49	37·36	37·23	37·10	36·97	36·84	36·71	36·59	36·46	36·34
40	38·45	38·32	38·15	38·05	37·92	37·79	37·66	37·53	37·40	37·27
41	39·41	39·28	39·14	39·00	38·87	38·73	38·60	38·47	38·34	38·20
42	40·37	40·24	40·09	39·95	39·82	39·68	39·54	39·41	39·27	39·13
43	41·33	41·19	41·05	40·90	40·76	40·62	40·48	40·35	40·21	40·07
44	42·30	42·15	42·00	41·86	41·71	41·57	41·43	41·28	41·14	41·00
45	43·26	43·11	42·95	42·81	42·66	42·51	42·37	42·22	42·08	41·93
46	44·29	44·07	43·91	43·76	43·61	43·46	43·31	43·16	43·01	42·86
47	45·18	45·03	44·86	44·71	44·56	44·40	44·25	44·10	43·94	43·79
48	46·14	45·98	45·82	45·66	45·50	45·35	45·19	45·04	44·88	44·72
49	47·10	46·94	46·77	46·61	46·45	46·29	46·13	45·97	45·81	45·65
50	48·07	47·90	47·73	47·57	47·40	47·24	47·07	46·91	46·75	46·59

Table for reducing the Volume of a Gas to 0° C.—*Continued.*

0°	11°	12°	13°	14°	15°	16°	17°	18°	19°	20°
51	49·03	48·86	48·69	48·52	48·35	48·18	48·01	47·85	47·68	47·52
52	49·99	49·82	49·64	49·47	49·30	49·13	48·95	48·79	48·62	48·45
53	50·95	50·77	50·59	50·42	50·24	50·07	49·89	49·72	49·55	49·38
54	51·91	51·73	51·55	51·37	51·19	51·02	50·84	50·66	50·49	50·32
55	52·87	52·69	52·50	52·33	52·14	51·96	51·78	51·60	51·43	51·25
56	53·84	53·65	53·46	53·28	53·09	52·91	52·72	52·54	52·36	52·18
57	54·80	54·61	54·41	54·23	54·04	53·86	53·66	53·48	53·29	53·11
58	55·76	55·56	55·37	55·18	54·98	54·80	54·60	54·42	54·23	54·04
59	56·72	56·52	56·32	56·13	55·93	55·74	55·54	55·35	55·16	54·97
60	57·68	57·47	57·28	57·08	56·88	56·68	56·48	56·29	56·09	55·91
61	58·64	58·43	58·23	58·03	57·83	57·63	57·42	57·23	57·02	56·84
62	59·60	59·39	59·19	58·98	58·78	58·57	58·36	58·17	57·96	57·77
63	60·56	60·35	60·14	59·93	59·72	59·52	59·30	59·11	58·90	58·71
64	61·53	61·31	61·10	60·88	60·67	60·46	60·25	60·04	59·83	59·64
65	62·49	62·26	62·05	61·84	61·62	61·40	61·19	60·98	60·77	60·57
66	63·45	63·22	63·01	62·79	62·57	62·35	62·13	61·92	61·70	61·50
67	64·41	64·18	63·96	63·74	63·52	63·29	63·07	62·86	62·63	62·43
68	65·37	65·13	64·92	64·69	64·46	64·23	64·01	63·80	63·57	63·36
69	66·33	66·09	65·87	65·64	65·41	65·18	64·95	64·73	64·50	64·30
70	67·29	67·05	66·82	66·59	66·36	66·13	65·90	65·67	65·44	65·23
71	68·25	68·01	67·77	67·54	67·31	67·07	66·84	66·61	66·38	66·16
72	69·21	68·97	68·73	68·49	68·26	68·02	67·78	67·55	67·31	67·09
73	70·17	69·92	69·68	69·44	69·20	68·96	68·72	68·49	68·26	68·03
74	71·14	70·88	70·64	70·40	70·15	69·91	69·66	69·42	69·18	68·96
75	72·10	71·84	71·59	71·35	71·10	70·85	70·61	70·37	70·12	69·89
76	73·06	72·80	72·55	72·30	72·05	71·80	71·55	71·30	71·05	70·82
77	74·02	73·76	73·51	73·25	73·00	72·74	72·49	72·24	71·98	71·75
78	74·98	74·71	74·46	74·20	73·94	73·69	73·43	73·18	72·92	72·68
79	75·94	75·67	75·41	75·15	74·89	74·63	74·37	74·11	73·85	73·61
80	76·90	76·63	76·37	76·10	75·84	75·58	75·31	75·06	74·79	74·54
81	77·86	77·59	77·32	77·05	76·79	76·52	76·25	76·00	75·73	75·47
82	78·82	78·55	78·28	78·00	77·74	77·47	77·19	76·94	76·66	76·40
83	79·78	79·50	79·23	78·95	78·68	78·41	78·13	77·87	77·60	77·34
84	80·75	80·46	80·19	79·91	79·63	79·35	79·08	78·81	78·53	78·27
85	81·71	81·42	81·14	80·86	80·58	80·30	80·02	79·75	79·47	79·20
86	82·67	82·38	82·10	81·81	81·53	81·24	80·96	80·69	80·40	80·13
87	83·63	83·33	83·05	82·76	82·48	82·19	81·90	81·63	81·33	81·06
88	84·59	84·29	84·01	83·71	83·42	83·13	82·84	82·57	82·27	81·99
89	85·56	85·25	84·96	84·66	84·37	84·08	83·78	83·50	83·22	82·93
90	86·52	86·21	85·92	85·62	85·32	85·02	84·72	84·44	84·14	83·86
91	87·48	87·17	86·87	86·57	86·27	85·96	85·66	85·38	85·07	84·79
92	88·44	88·13	87·83	87·52	87·22	86·91	86·60	86·32	86·01	85·72
93	89·40	89·08	88·78	88·47	88·16	87·85	87·54	87·25	86·95	86·66
94	90·36	90·04	89·73	89·42	89·11	88·80	88·49	88·19	87·88	87·59
95	91·33	91·00	90·68	90·38	90·06	89·74	89·43	89·13	88·82	88·52
96	92·29	91·96	91·64	91·33	91·01	90·69	90·37	90·07	89·75	89·45
97	93·25	92·92	92·59	92·28	91·96	91·63	91·31	91·00	90·68	90·38
98	94·21	93·87	93·55	93·23	92·90	92·58	92·25	91·94	91·62	91·31
99	95·17	94·83	94·50	94·18	93·85	93·52	93·19	92·88	92·55	92·24
100	96·13	95·79	95·46	95·13	94·80	94·47	94·14	93·82	93·49	93·18

Table for reducing the Volume of a Gas to 0° C.—*Continued.*

0°	21°	22°	23°	24°	25°	26°	27°	28°	29°
1	0·929	0·926	0·922	0·919	0·916	0·913	0·910	0·907	0·904
2	1·857	1·851	1·845	1·839	1·832	1·826	1·820	1·814	1·808
3	2·786	2·777	2·767	2·758	2·749	2·739	2·730	2·721	2·712
4	3·714	3·702	3·690	3·677	3·665	3·652	3·640	3·628	3·616
5	4·643	4·628	4·612	4·597	4·581	4·566	4·551	4·535	4·520
6	5·572	5·553	5·534	5·516	5·497	5·479	5·461	5·442	5·424
7	6·500	6·479	6·457	6·435	6·413	6·392	6·371	6·349	6·328
8	7·429	7·404	7·379	7·354	7·330	7·305	7·281	7·256	7·232
9	8·357	8·330	8·302	8·274	8·246	8·218	8·191	8·163	8·136
10	9·286	9·255	9·224	9·193	9·162	9·131	9·101	9·070	9·040
11	10·21	10·18	10·15	10·11	10·07	10·04	10·01	9·98	9·94
12	11·14	11·11	11·07	11·03	10·99	10·96	10·92	10·88	10·85
13	12·07	12·03	11·99	11·95	11·91	11·87	11·83	11·79	11·75
14	13·00	12·96	12·91	12·87	12·83	12·78	12·74	12·70	12·66
15	13·93	13·88	13·84	13·79	13·74	13·70	13·65	13·61	13·56
16	14·86	14·81	14·76	14·71	14·66	14·61	14·56	14·51	14·46
17	15·79	15·73	15·68	15·63	15·58	15·52	15·47	15·42	15·37
18	16·71	16·66	16·60	16·55	16·49	16·44	16·38	16·33	16·27
19	17·64	17·58	17·53	17·47	17·41	17·35	17·29	17·23	17·18
20	18·57	18·51	18·45	18·39	18·32	18·26	18·20	18·14	18·08
21	19·50	19·43	19·37	19·31	19·24	19·17	19·11	19·05	18·98
22	20·43	20·36	20·29	20·23	20·15	20·09	20·02	19·95	19·89
23	21·36	21·29	21·21	21·15	21·07	21·00	20·93	20·86	20·79
24	22·28	22·21	22·14	22·07	21·99	21·91	21·84	21·77	21·70
25	23·21	23·14	23·06	22·99	22·90	22·83	22·75	22·68	22·60
26	24·14	24·06	23·98	23·91	23·82	23·74	23·66	23·58	23·50
27	25·07	24·99	24·90	24·83	24·73	24·65	24·57	24·49	24·41
28	26·00	25·91	25·82	25·74	25·65	25·57	25·48	25·40	25·31
29	26·93	26·84	26·75	26·67	26·57	26·48	26·39	26·30	26·22
30	27·86	27·77	27·67	27·58	27·49	27·39	27·30	27·21	27·12
31	28·79	28·70	28·59	28·50	28·41	28·30	28·21	28·12	28·02
32	29·72	29·62	29·51	29·42	29·32	29·22	29·12	29·02	28·93
33	30·65	30·55	30·44	30·34	30·24	30·13	30·03	29·93	29·83
34	31·57	31·47	31·36	31·26	31·16	31·04	30·94	30·84	30·74
35	32·50	32·40	32·28	32·18	32·07	31·96	31·85	31·75	31·64
36	33·43	33·32	33·20	33·10	32·99	32·87	32·76	32·65	32·54
37	34·36	34·25	34·12	34·02	33·90	33·78	33·67	33·56	33·45
38	35·29	35·17	35·05	34·93	34·82	34·70	34·58	34·47	34·35
39	36·22	36·10	35·97	35·85	35·74	35·61	35·49	35·37	35·26
40	37·14	37·02	36·90	36·77	36·65	36·52	36·40	36·28	36·16
41	38·07	37·95	37·82	37·69	37·57	37·43	37·31	37·19	37·06
42	39·00	38·87	38·74	38·61	38·48	38·35	38·22	38·09	37·97
43	39·93	39·80	39·66	39·53	39·40	39·26	39·13	39·00	38·87
44	40·85	40·72	40·59	40·45	40·32	40·17	40·04	39·91	39·78
45	41·78	41·65	41·51	41·37	41·23	41·09	40·95	40·82	40·68
46	42·71	42·57	42·43	42·29	42·15	42·00	41·86	41·72	41·58
47	43·64	43·50	43·35	43·21	43·06	42·91	42·77	42·63	42·49
48	44·57	44·42	44·27	44·12	43·98	43·83	43·68	43·54	43·39
49	45·50	45·35	45·19	45·04	44·89	44·74	44·59	44·44	44·30
50	46·43	46·28	46·12	45·97	45·81	45·66	45·51	45·35	45·20

Table for reducing the Volume of a Gas to 0° C.—*Continued.*

0°	21°	22°	23°	24°	25°	26°	27°	28°	29°
51	47·36	47·20	47·04	46·89	46·73	46·57	46·42	46·26	46·10
52	48·29	48·13	47·96	47·81	47·64	47·49	47·33	47·16	47·01
53	49·22	49·06	48·89	48·73	48·56	48·40	48·24	48·07	47·91
54	50·14	49·98	49·81	49·65	49·48	49·31	49·15	48·98	48·82
55	51·07	50·91	50·73	50·57	50·39	50·23	50·06	49·89	49·72
56	52·00	51·83	51·65	51·49	51·31	51·14	50·97	50·79	50·62
57	52·93	52·76	52·58	52·41	52·22	52·05	51·88	51·70	51·53
58	53·86	53·68	53·50	53·32	53·14	52·97	52·79	52·61	52·43
59	54·79	54·61	54·42	54·24	54·06	53·88	53·70	53·51	53·34
60	55·72	55·53	55·34	55·16	54·97	54·79	54·61	54·42	54·24
61	56·65	56·46	56·26	56·08	55·89	55·70	55·52	55·33	55·14
62	57·58	57·38	57·19	57·00	56·80	56·62	56·43	56·23	56·05
63	58·51	58·31	58·11	57·92	57·72	57·53	57·34	57·14	56·95
64	59·42	59·23	59·03	58·84	58·64	58·44	58·25	58·05	57·86
65	60·36	60·16	59·95	59·76	59·55	59·36	59·16	58·96	58·76
66	61·29	61·08	60·87	60·68	60·47	60·27	60·07	59·86	59·66
67	62·22	62·01	61·79	61·60	61·38	61·18	60·98	60·77	60·57
68	63·15	62·93	62·72	62·51	62·30	62·10	61·89	61·68	61·47
69	64·08	63·86	63·64	63·43	63·22	63·01	62·80	62·58	62·38
70	65·00	64·79	64·57	64·35	64·13	63·92	63·71	63·49	63·28
71	65·93	65·71	65·49	65·27	65·05	64·83	64·62	64·40	64·18
72	66·86	66·64	66·42	66·19	65·96	65·75	65·53	65·30	65·09
73	67·79	67·57	67·34	67·11	66·88	66·66	66·44	66·21	65·99
74	68·81	68·49	68·26	68·03	67·80	67·57	67·35	67·12	66·90
75	69·64	69·42	69·18	68·95	68·71	68·49	68·26	68·03	67·80
76	70·57	70·34	70·10	69·87	69·63	69·40	69·17	68·93	68·70
77	71·50	71·27	71·03	70·79	70·54	70·31	70·08	69·84	69·61
78	72·43	72·19	71·95	71·70	71·46	71·22	70·99	70·75	70·51
79	73·36	73·12	72·87	72·62	72·38	72·14	71·90	71·65	71·42
80	74·29	74·04	73·79	73·54	73·30	73·05	72·81	72·56	72·32
81	75·22	74·97	74·71	74·46	74·22	73·96	73·72	73·47	73·22
82	76·15	75·89	75·63	75·38	75·13	74·88	74·63	74·37	74·13
83	77·08	76·82	76·56	76·30	76·05	75·79	75·54	75·28	75·03
84	78·00	77·74	77·48	77·22	76·96	76·70	76·45	76·19	75·94
85	78·93	78·67	78·40	78·14	77·88	77·62	77·36	77·10	76·84
86	79·86	79·59	79·32	79·06	78·80	78·53	78·27	78·00	77·74
87	80·79	80·52	80·25	79·98	79·71	79·44	79·18	78·91	78·65
88	81·72	81·44	81·17	80·90	80·63	80·36	80·09	79·82	79·55
89	82·65	82·37	82·09	81·82	81·55	81·27	81·00	80·72	80·46
90	83·57	83·30	83·02	82·74	82·46	82·18	81·91	81·63	81·36
91	84·50	84·22	83·94	83·66	83·38	83·09	82·82	82·54	82·26
92	85·43	85·15	84·86	84·58	84·29	84·01	83·73	83·44	83·17
93	86·36	86·08	85·79	85·50	85·21	84·92	84·64	84·35	84·07
94	87·28	87·00	86·71	86·42	86·13	85·83	85·55	85·26	84·98
95	88·21	87·93	87·63	87·34	87·04	86·75	86·46	86·17	85·88
96	89·14	88·85	88·55	88·26	87·96	87·66	87·37	87·07	86·78
97	90·07	89·78	89·48	89·18	88·87	88·57	88·28	87·98	87·69
98	91·00	90·70	90·40	90·09	89·79	89·48	89·19	88·89	88·59
99	91·93	91·63	91·32	91·01	90·71	90·40	90·10	89·79	89·50
100	92·86	92·55	92·24	91·93	91·62	91·31	91·01	90·70	90·40

TABLE III.

Table for reducing the Volume of a Gas to 760 mm. Pressure.

For temperatures between 0° and 12°, deduct 1 mm. from the barometer pressure; between 13° and 19°, 2 mm.; between 20° and 25°, 3 mm.

760	710	712	714	716	718	720	722	724	726	728
1	0·934	0·937	0·940	0·942	0·945	0·947	0·950	0·953	0·955	0·958
2	1·868	1·874	1·879	1·884	1·890	1·895	1·900	1·905	1·911	1·916
3	2·803	2·810	2·818	2·826	2·834	2·842	2·850	2·858	2·866	2·874
4	3·738	3·747	3·758	3·768	3·779	3·789	3·800	3·810	3·821	3·832
5	4·672	4·685	4·697	4·711	4·724	4·736	4·750	4·763	4·777	4·790
6	5·607	5·621	5·637	5·653	5·669	5·684	5·700	5·716	5·732	5·747
7	6·540	6·558	6·577	6·595	6·614	6·631	6·650	6·668	6·687	6·705
8	7·474	7·494	7·516	7·537	7·558	7·578	7·600	7·621	7·642	7·663
9	8·409	8·431	8·456	8·479	8·503	8·526	8·550	8·573	8·598	8·621
10	9·34	9·37	9·40	9·42	9·45	9·47	9·50	9·53	9·55	9·58
11	10·28	10·31	10·34	10·36	10·39	10·42	10·45	10·48	10·51	10·54
12	11·21	11·24	11·27	11·30	11·34	11·37	11·40	11·43	11·46	11·50
13	12·14	12·18	12·21	12·24	12·28	12·31	12·35	12·38	12·41	12·45
14	13·08	13·12	13·16	13·19	13·23	13·26	13·30	13·34	13·37	13·41
15	14·02	14·06	14·10	14·13	14·17	14·21	14·25	14·29	14·33	14·37
16	14·95	14·99	15·03	15·07	15·11	15·15	15·20	15·24	15·28	15·33
17	15·88	15·93	15·98	16·02	16·06	16·10	16·15	16·19	16·23	16·28
18	16·82	16·87	16·92	16·96	17·01	17·05	17·10	17·15	17·19	17·24
19	17·76	17·81	17·86	17·90	17·95	18·00	18·05	18·10	18·15	18·21
20	18·68	18·74	18·79	18·84	18·90	18·95	19·00	19·05	19·11	19·16
21	19·62	19·68	19·73	19·78	19·84	19·90	19·95	20·00	20·06	20·12
22	20·55	20·61	20·67	20·72	20·78	20·84	20·90	20·96	21·01	21·07
23	21·49	21·55	21·61	21·66	21·73	21·79	21·85	21·91	21·97	22·03
24	22·43	22·49	22·55	22·61	22·68	22·74	22·80	22·86	22·92	22·99
25	23·35	23·42	23·49	23·55	23·62	23·69	23·75	23·81	23·88	23·95
26	24·29	24·36	24·43	24·50	24·57	24·64	24·70	24·77	24·83	24·90
27	25·23	25·30	25·37	25·44	25·51	25·58	25·65	25·72	25·79	25·86
28	26·16	26·23	26·30	26·37	26·45	26·53	26·60	26·67	26·74	26·82
29	27·10	27·17	27·24	27·31	27·40	27·48	27·55	27·62	27·70	26·78
30	28·03	28·10	28·18	28·26	28·34	28·42	28·50	28·58	28·66	28·74
31	28·97	29·04	29·12	29·20	29·29	29·37	29·45	29·53	29·62	29·70
32	29·90	29·98	30·06	30·14	30·23	30·32	30·40	30·48	30·57	30·66
33	30·83	30·91	31·00	31·08	31·17	31·26	31·35	31·43	31·52	31·61
34	31·77	31·85	31·94	32·03	32·12	32·21	32·30	32·39	32·48	32·57
35	32·71	32·79	32·88	32·97	33·07	33·16	33·25	33·34	33·44	33·53
36	33·64	33·73	33·82	33·91	34·01	34·10	34·20	34·29	34·39	34·49
37	34·57	34·66	34·76	34·86	34·96	35·05	35·15	35·25	35·35	35·45
38	35·50	35·60	35·70	35·80	35·90	36·00	36·10	36·20	36·30	36·40
39	36·44	36·54	36·64	36·74	36·85	36·95	37·05	37·15	37·26	37·37
40	37·38	37·48	37·58	37·68	37·79	37·89	38·00	38·10	38·21	38·32
41	38·31	38·41	38·52	38·62	38·74	38·84	38·95	39·05	39·17	39·28
42	39·23	39·35	39·46	39·57	39·69	39·79	39·90	40·01	40·12	40·23
43	40·18	40·29	40·40	40·51	40·62	40·73	40·85	40·96	41·08	41·19
44	41·11	41·22	41·34	41·44	41·56	41·68	41·80	41·91	42·03	42·16
45	42·05	42·16	42·28	42·39	42·52	42·63	42·75	42·87	42·99	43·11
46	42·98	43·10	43·22	43·34	43·46	43·58	43·70	43·82	43·94	44·06
47	43·91	44·03	44·15	44·27	44·40	44·52	44·65	44·77	44·90	45·03
48	44·84	44·96	45·09	45·22	45·35	45·47	45·60	45·72	45·85	45·98
49	45·78	45·91	46·04	46·17	46·30	46·42	46·55	46·67	46·80	46·94
50	46·72	46·85	46·97	47·11	47·24	47·36	47·50	47·63	47·77	47·90

Table for reducing the Volume of a Gas to 760 mm.—*Continued.*

760	710	712	714	716	718	720	722	724	726	728
51	47·65	47·79	47·92	48·05	48·18	48·31	48·45	48·59	48·73	48·86
52	48·58	48·72	48·85	48·99	49·13	49·26	49·40	49·54	49·68	49·82
53	49·52	49·66	49·79	49·93	50·07	50·21	50·35	50·48	50·64	50·78
54	50·45	50·59	50·73	50·87	51·01	51·15	51·30	51·44	51·59	51·73
55	51·38	51·53	51·67	51·82	51·96	52·10	52·25	52·39	52·54	52·69
56	52·32	52·47	52·61	52·76	52·91	53·05	53·20	53·35	53·50	53·65
57	53·25	53·41	53·55	53·70	53·85	54·00	54·15	54·30	54·45	54·60
58	54·19	54·34	54·49	54·64	54·79	54·94	55·10	55·25	55·41	55·56
59	55·13	55·28	55·43	55·59	55·74	55·89	56·05	56·21	56·37	56·52
60	56·07	56·22	56·37	56·53	56·69	56·84	57·00	57·16	57·32	57·47
61	57·00	57·15	57·31	57·47	57·63	57·79	57·95	58·11	58·27	58·43
62	57·93	58·09	58·25	58·41	58·58	58·74	58·90	59·06	59·23	59·39
63	58·87	59·03	59·19	59·35	59·52	59·68	59·85	60·01	60·18	60·35
64	59·80	59·96	60·13	60·30	60·47	60·63	60·80	60·97	61·14	61·30
65	60·74	60·90	61·07	61·24	61·41	61·58	61·75	61·92	62·09	62·26
66	61·67	61·84	62·01	62·18	62·35	62·52	62·70	62·87	63·05	63·22
67	62·60	62·77	62·95	63·12	63·30	63·47	63·65	63·82	64·00	64·18
68	63·54	63·71	63·89	64·06	64·24	64·42	64·60	64·78	64·96	65·13
69	64·47	64·65	64·83	65·01	65·19	65·37	65·55	65·73	65·91	66·09
70	65·40	65·58	65·77	65·95	66·14	66·32	66·50	66·68	66·87	67·05
71	66·34	66·52	66·71	66·89	67·08	67·26	67·45	67·63	67·82	68·01
72	67·27	67·46	67·65	67·83	68·02	68·21	68·40	68·59	68·78	68·97
73	68·20	68·39	68·58	68·77	68·97	69·16	69·35	69·54	69·73	69·92
74	69·14	69·33	69·53	69·72	69·92	70·11	70·30	70·49	70·69	70·88
75	70·07	70·27	70·47	70·66	70·86	71·05	71·25	71·44	71·64	71·84
76	71·01	71·21	71·41	71·60	71·80	72·00	72·20	72·40	72·60	72·80
77	71·94	72·14	72·34	72·54	72·75	72·95	73·15	73·35	73·55	73·75
78	72·87	73·07	73·28	73·48	73·69	73·89	74·10	74·30	74·51	74·71
79	73·80	74·01	74·22	74·42	74·63	74·84	75·05	75·25	75·46	75·67
80	74·74	74·94	75·16	75·37	75·58	75·78	76·00	76·21	76·42	76·63
81	75·67	75·88	76·10	76·31	76·53	76·74	76·95	77·16	77·37	77·58
82	76·60	76·82	77·04	77·25	77·47	77·68	77·90	78·11	78·33	78·54
83	77·54	77·76	77·98	78·19	78·41	78·63	78·85	79·07	79·28	79·50
84	78·47	78·69	78·91	79·13	79·35	79·57	79·80	80·02	80·24	80·46
85	79·41	79·63	79·86	80·08	80·31	80·53	80·75	80·97	81·19	81·41
86	80·34	80·57	80·80	81·02	81·25	81·47	81·70	81·92	82·15	82·37
87	81·28	81·50	81·74	81·96	82·19	82·42	82·65	82·87	83·10	83·33
88	82·21	82·44	82·68	82·90	83·13	83·36	83·60	83·83	84·06	84·29
89	83·15	83·38	83·62	83·85	84·08	84·31	84·55	84·78	85·02	85·25
90	84·09	84·31	84·56	84·79	85·03	85·26	85·50	85·73	85·98	86·21
91	85·02	85·25	85·50	85·73	85·98	86·21	86·45	86·69	86·93	87·17
92	85·95	86·19	86·44	86·68	86·92	87·16	87·40	87·64	87·89	88·13
93	86·89	87·12	87·38	87·62	87·87	88·11	88·35	88·59	88·84	89·08
94	87·82	88·06	88·32	88·56	88·81	89·05	89·30	89·54	89·80	90·04
95	88·76	89·01	89·26	89·50	89·75	90·00	90·25	90·50	90·75	91·00
96	89·69	89·94	90·20	90·45	90·70	90·95	91·20	91·45	91·70	91·95
97	90·62	90·87	91·13	91·38	91·64	91·89	92·15	92·40	92·66	92·91
98	91·56	91·82	92·07	92·33	92·59	92·84	93·10	93·35	93·62	93·87
99	92·49	92·75	93·01	93·26	93·53	93·79	94·05	94·31	94·57	94·83
100	93·42	93·68	93·95	94·21	94·47	94·74	95·00	95·26	95·53	95·79

Table for reducing the Volume of a Gas to 760 mm.—*Continued.*

760	730	732	734	736	738	740	742	744	746	748
1	0·961	0·963	0·966	0·968	0·971	0·974	0·976	0·979	0·982	0·984
2	1·921	1·926	1·932	1·937	1·942	1·947	1·953	1·958	1·963	1·968
3	2·882	2·889	2·898	2·905	2·913	2·921	2·929	2·937	2·945	2·953
4	3·842	3·852	3·864	3·874	3·884	3·895	3·905	3·916	3·926	3·937
5	4·803	4·816	4·830	4·842	4·855	4·868	4·882	4·895	4·908	4·921
6	5·763	5·779	5·796	5·810	5·826	5·842	5·858	5·874	5·890	5·905
7	6·724	6·742	6·762	6·779	6·797	6·816	6·834	6·853	6·871	6·889
8	7·684	7·705	7·728	7·747	7·768	7·790	7·810	7·832	7·853	7·874
9	8·645	8·668	8·693	8·716	8·739	8·763	8·787	8·811	8·834	8·858
10	9·61	9·63	9·66	9·68	9·71	9·74	9·76	9·79	9·82	9·84
11	10·57	10·59	10·62	10·65	10·68	10·71	10·74	10·77	10·80	10·82
12	11·53	11·56	11·59	11·62	11·65	11·68	11·71	11·75	11·78	11·81
13	12·49	12·52	12·55	12·59	12·62	12·66	12·69	12·73	12·76	12·79
14	13·45	13·48	13·52	13·56	13·59	13·63	13·66	13·70	13·74	13·78
15	14·41	14·44	14·48	14·52	14·56	14·60	14·64	14·69	14·73	14·77
16	15·37	15·41	15·45	15·49	15·53	15·58	15·62	15·67	15·71	15·75
17	16·33	16·37	16·41	16·46	16·50	16·55	16·60	16·65	16·69	16·73
18	17·29	17·33	17·38	17·43	17·47	17·52	17·57	17·62	17·67	17·72
19	18·25	18·29	18·36	18·40	18·45	18·50	18·55	18·60	18·65	18·70
20	19·21	19·26	19·32	19·37	19·42	19·47	19·53	19·58	19·63	19·68
21	20·17	20·22	20·28	20·34	20·39	20·44	20·50	20·56	20·61	20·66
22	21·13	21·19	21·25	21·31	21·36	21·42	21·48	21·54	21·59	21·65
23	22·09	22·15	22·21	22·27	22·33	22·39	22·45	22·51	22·57	22·64
24	23·05	23·11	23·18	23·24	23·30	23·36	23·43	23·50	23·56	23·63
25	24·01	24·07	24·14	24·21	24·27	24·34	24·41	24·48	24·54	24·61
26	24·97	25·04	25·11	25·18	25·24	25·31	25·38	25·45	25·52	25·59
27	25·93	26·00	26·07	26·14	26·21	26·28	26·36	26·43	26·50	26·58
28	26·89	26·96	27·04	27·12	27·18	27·26	27·33	27·41	27·48	27·56
29	27·85	27·92	28·00	28·08	28·15	28·23	28·31	28·39	28·47	28·55
30	28·82	28·89	28·97	29·05	29·13	29·21	29·29	29·37	29·45	29·53
31	29·78	29·86	29·94	30·02	30·10	30·18	30·26	30·35	30·43	30·51
32	30·74	30·82	30·91	30·99	31·07	31·15	31·24	31·33	31·41	31·50
33	31·71	31·78	31·87	31·96	32·04	32·13	32·21	32·30	32·39	32·48
34	32·66	32·75	32·84	32·93	33·01	33·10	33·19	33·28	33·37	33·46
35	33·62	33·71	33·80	33·89	33·38	34·07	34·17	34·27	34·36	34·45
36	34·58	34·67	34·77	34·86	34·95	35·05	35·15	35·25	35·34	35·43
37	35·54	35·63	35·73	35·83	35·92	36·02	36·12	36·22	36·32	36·42
38	36·50	36·60	36·70	36·80	36·90	37·00	37·10	37·20	37·30	37·40
39	37·47	37·57	37·67	37·77	37·87	37·97	38·07	38·18	38·28	38·39
40	38·42	38·52	38·64	38·74	38·84	38·95	39·05	39·16	39·26	39·37
41	39·38	39·48	39·60	39·71	39·81	39·92	40·02	40·14	40·24	40·36
42	40·34	40·44	40·56	40·68	40·78	40·89	41·00	41·12	41·22	41·34
43	41·30	41·46	41·53	41·64	41·75	41·86	41·97	42·10	42·20	42·32
44	42·27	42·38	42·50	42·62	42·73	42·84	42·95	43·07	43·18	43·30
45	43·22	43·34	43·46	43·58	43·69	43·81	43·93	44·06	44·17	44·29
46	44·18	44·30	44·42	44·54	44·66	44·78	44·90	45·03	45·15	45·27
47	45·15	45·26	45·39	45·52	45·64	45·76	45·88	46·01	46·13	46·26
48	46·10	46·23	46·36	46·49	46·61	46·73	46·85	46·99	47·12	47·24
49	47·06	47·19	47·32	47·44	47·57	47·70	47·83	47·97	48·10	48·23
50	48·03	48·18	48·30	48·42	48·55	48·68	48·82	48·95	49·08	49·21

Table for reducing the Volume of a Gas to 760 mm.—*Continued.*

760	730	732	734	736	738	740	742	744	746	748
51	48·99	49·12	49·26	49·39	49·52	49·65	49·79	49·93	50·06	50·19
52	49·96	50·08	50·22	50·36	50·49	50·63	50·77	50·91	51·04	51·18
53	50·91	51·05	51·19	51·33	51·46	51·60	51·75	51·89	52·02	52·16
54	51·87	52·01	52·16	52·30	52·44	52·58	52·72	52·87	53·01	53·15
55	52·83	52·98	53·13	53·27	53·41	53·55	53·70	53·85	53·99	54·14
56	53·79	53·94	54·09	54·23	54·37	54·52	54·68	54·83	54·97	55·11
57	54·75	54·90	55·05	55·20	55·35	55·50	55·65	55·80	55·95	56·10
58	55·71	55·86	56·02	56·17	56·32	56·47	56·63	56·78	56·93	57·08
59	56·67	56·83	56·99	57·14	57·29	57·44	57·60	57·76	57·92	58·07
60	57·63	57·79	57·95	58·10	58·26	58·42	58·58	58·74	58·90	59·05
61	58·59	58·75	58·91	59·07	59·23	59·39	59·56	59·72	59·88	60·04
62	59·55	59·72	59·88	60·04	60·20	60·36	60·53	60·70	60·86	61·02
63	60·51	60·68	60·85	61·01	61·17	61·34	61·51	61·68	61·84	62·00
64	61·47	61·64	61·81	61·98	62·15	62·32	62·49	62·66	62·82	62·99
65	62·43	62·60	62·77	62·94	63·11	63·28	63·46	63·64	63·81	63·98
66	63·39	63·57	63·74	63·91	64·08	64·26	64·44	64·62	64·79	64·96
67	64·35	64·53	64·71	64·88	65·05	65·23	65·41	65·59	65·77	65·94
68	65·31	65·50	65·68	65·85	66·02	66·20	66·38	66·56	66·74	66·92
69	66·27	66·45	66·64	66·82	67·00	67·18	67·37	67·55	67·73	67·91
70	67·24	67·42	67·61	67·79	67·97	68·16	68·34	68·53	68·71	68·89
71	68·20	68·39	68·58	68·76	68·94	69·13	69·32	69·51	69·69	69·88
72	69·16	69·35	69·54	69·73	69·92	70·11	70·80	70·49	70·68	70·86
73	70·12	70·31	70·51	70·69	70·88	71·08	71·27	71·47	71·66	71·85
74	71·08	71·28	71·48	71·66	71·85	72·05	72·25	72·45	72·64	72·83
75	72·04	72·24	72·44	72·63	72·82	73·02	73·22	73·42	73·62	73·82
76	73·00	73·20	73·40	73·60	73·80	74·00	74·20	74·40	74·60	74·80
77	73·96	74·17	74·37	74·57	74·77	74·97	75·18	75·39	75·59	75·79
78	74·92	75·12	75·33	75·53	75·74	75·95	76·16	76·37	76·57	76·77
79	75·88	76·09	76·30	76·50	76·71	76·92	77·13	77·34	77·55	77·55
80	76·84	77·05	77·27	77·47	77·68	77·90	78·10	78·32	78·53	78·74
81	77·80	78·02	78·23	78·44	78·65	78·87	79·08	79·30	79·51	79·72
82	78·76	78·98	79·20	79·41	79·62	79·84	80·06	80·28	80·50	80·71
83	79·72	79·94	80·16	80·38	80·60	80·82	81·04	81·26	81·48	81·69
84	80·68	80·90	81·12	81·34	81·56	81·79	82·01	82·24	82·46	82·68
85	81·64	81·87	82·10	82·31	82·53	82·76	82·99	83·22	83·44	83·66
86	82·60	82·83	83·06	83·28	83·50	83·73	83·97	84·20	84·42	84·64
87	83·56	83·79	84·02	84·25	84·48	84·71	84·94	85·17	85·40	85·62
88	84·52	84·76	85·00	85·22	85·45	85·68	85·92	86·15	86·38	86·61
89	85·48	85·72	85·96	86·19	86·42	86·66	86·89	87·13	87·36	87·59
90	86·45	86·68	86·93	87·16	87·39	87·63	87·87	88·11	88·34	88·58
91	87·41	87·65	87·89	88·12	88·36	88·61	88·85	89·09	89·33	89·56
92	88·37	88·61	88·86	89·09	89·33	89·58	89·82	90·07	90·31	90·55
93	89·33	89·57	89·82	90·06	90·30	90·55	90·80	91·05	91·29	91·53
94	90·29	90·54	90·79	91·03	91·27	91·53	91·78	92·03	92·27	92·51
95	91·25	91·50	91·75	92·00	92·25	92·50	92·75	93·00	93·25	93·50
96	92·21	92·46	92·72	92·97	93·22	93·47	93·73	93·98	94·23	94·48
97	93·17	93·43	93·68	93·93	94·19	94·45	94·71	94·96	95·22	95·47
98	94·13	94·39	94·65	94·90	95·16	95·42	95·68	95·94	96·20	96·45
99	95·09	95·35	95·61	95·87	96·13	96·39	96·66	96·92	97·18	97·43
100	96·05	96·32	96·58	96·84	97·11	97·37	97·63	97·89	98·16	98·42

Table for reducing the Volume of a Gas to 760 mm.—*Continued.*

760	750	752	754	756	758	762	764	766	768	770
1	0·987	0·989	0·992	0·995	0·997	1·003	1·005	1·008	1·011	1·013
2	1·974	1·979	1·984	1·989	1·995	2·005	2·011	2·016	2·021	2·026
3	2·960	2·968	2·976	2·984	2·992	3·007	3·016	3·024	3·032	3·039
4	3·947	3·958	3·968	3·979	3·990	4·010	4·021	4·032	4·042	4·052
5	4·934	4·947	4·960	4·974	4·987	5·013	5·026	5·040	5·053	5·066
6	5·921	5·937	5·952	5·968	5·984	6·016	6·032	6·047	6·063	6·079
7	6·908	6·926	6·944	6·963	6·982	7·018	7·037	7·055	7·074	7·092
8	7·984	7·916	7·936	7·958	7·979	8·021	8·042	8·063	8·084	8·106
9	8·881	8·905	8·929	8·952	8·977	9·023	9·048	9·071	9·095	9·119
10	9·87	9·89	9·92	9·95	9·97	10·03	10·05	10·08	10·11	10·13
11	10·85	10·88	10·91	10·94	10·97	11·03	11·06	11·09	11·12	11·14
12	11·84	11·87	11·90	11·94	11·97	12·04	12·07	12·10	12·13	12·16
13	12·83	12·86	12·89	12·93	12·96	13·04	13·07	13·10	13·14	13·17
14	13·82	13·85	13·88	13·92	13·96	14·04	14·07	14·11	14·15	14·17
15	14·81	14·84	14·87	14·92	14·96	15·04	15·08	15·12	15·16	15·19
16	15·79	15·83	15·87	15·91	15·95	16·05	16·09	16·13	16·17	16·21
17	16·78	16·82	16·86	16·91	16·95	17·05	17·09	17·14	17·18	17·22
18	17·77	17·81	17·85	17·90	17·95	18·05	18·10	18·15	18·19	18·23
19	18·75	18·80	18·85	18·90	18·95	19·05	19·10	19·15	19·20	19·25
20	19·74	19·79	19·84	19·89	19·95	20·05	20·11	20·16	20·21	20·26
21	20·72	20·77	20·83	20·89	20·94	21·05	21·11	21·17	21·22	21·27
22	21·71	21·76	21·82	21·88	21·94	22·06	22·12	22·18	22·23	22·28
23	22·70	22·75	22·81	22·88	22·94	23·06	23·12	23·18	23·24	23·30
24	23·69	23·74	23·80	23·87	23·93	24·06	24·13	24·19	24·25	24·31
25	24·67	24·73	24·80	24·87	24·93	25·06	25·13	25·20	25·26	25·32
26	25·66	25·72	25·79	25·86	25·93	26·06	26·14	26·21	26·27	26·34
27	26·65	26·71	26·78	26·86	26·93	27·07	27·15	27·22	27·28	27·35
28	27·63	27·70	27·77	27·85	27·92	28·07	28·15	28·23	28·29	28·36
29	28·62	28·69	28·76	28·84	28·92	29·07	29·16	29·24	29·30	29·37
30	29·60	29·68	29·76	29·84	29·92	30·07	30·16	30·24	30·32	30·39
31	30·59	30·67	30·75	30·84	30·92	31·08	31·17	31·25	31·33	31·41
32	31·58	31·66	31·74	31·83	31·92	32·08	32·17	32·26	32·34	32·42
33	32·56	32·65	32·73	32·82	32·91	33·08	33·18	33·27	33·35	33·43
34	33·55	33·64	33·73	33·82	33·91	34·09	34·18	34·28	34·36	34·45
35	34·54	34·63	34·72	34·82	34·91	35·09	35·19	35·28	35·37	35·46
36	35·52	35·62	35·71	35·81	35·91	36·09	36·19	36·29	36·38	36·47
37	36·51	36·61	36·71	36·81	36·90	37·09	37·20	37·30	37·39	37·49
38	37·50	37·60	37·70	37·80	37·90	38·10	38·20	38·30	38·40	38·50
39	38·49	38·59	38·69	38·80	38·90	39·10	39·21	39·31	39·41	39·51
40	39·47	39·58	39·68	39·79	39·90	40·10	40·21	40·32	40·42	40·52
41	40·46	40·56	40·67	40·79	40·89	41·11	41·22	41·33	41·43	41·54
42	41·44	41·55	41·66	41·78	41·89	42·11	42·22	42·34	42·44	42·55
43	42·43	42·54	42·66	42·78	42·89	43·11	43·23	43·35	43·45	43·56
44	43·42	43·53	43·65	43·77	43·89	44·12	44·23	44·35	44·46	44·58
45	44·40	44·52	44·64	44·76	44·88	45·12	45·24	45·36	45·47	45·59
46	45·39	45·51	45·63	45·76	45·88	46·12	46·24	46·36	46·48	46·60
47	46·38	46·50	46·63	46·76	46·88	47·12	47·25	47·38	47·49	47·61
48	47·36	47·49	47·62	47·75	47·87	48·13	48·25	48·39	48·51	48·63
49	48·35	48·48	48·61	48·74	48·87	49·13	49·26	49·40	49·52	49·64
50	49·34	49·47	49·60	49·74	49·87	50·13	50·26	50·40	50·53	50·66

Table for reducing the Volume of a Gas to 760 mm.—*Continued.*

760	750	752	754	756	758	762	764	766	768	770
51	50·33	50·46	50·60	50·74	50·87	51·14	51·27	51·41	51·54	51·67
52	51·32	51·45	51·59	51·73	51·87	52·14	52·28	52·42	52·55	52·68
53	52·30	52·44	52·58	52·73	52·87	53·14	53·28	53·42	53·56	53·70
54	53·29	53·43	53·57	53·72	53·86	54·14	54·28	54·43	54·57	54·72
55	54·28	54·42	54·56	54·71	54·86	55·15	55·29	55·44	55·58	55·73
56	55·26	55·41	55·56	55·71	55·86	56·15	56·29	56·45	56·59	56·74
57	56·25	56·40	56·55	56·70	56·85	57·15	57·30	57·45	57·60	57·76
58	57·24	57·39	57·54	57·69	57·85	58·15	58·30	58·46	58·61	58·77
59	58·22	58·38	58·53	58·69	58·85	59·16	59·31	59·47	59·62	59·78
60	59·21	59·37	59·52	59·68	59·84	60·16	60·32	60·47	60·63	60·79
61	60·20	60·36	60·52	60·68	60·84	61·16	61·32	61·48	61·64	61·81
62	61·19	61·35	61·51	61·67	61·84	62·16	62·33	62·49	62·65	62·82
63	62·17	62·34	62·50	62·67	62·83	63·17	63·33	63·50	63·67	63·84
64	63·16	63·33	63·49	63·66	63·83	64·17	64·34	64·51	64·68	64·85
65	64·15	64·32	64·49	64·66	64·83	65·17	65·34	65·51	65·69	65·86
66	65·13	65·31	65·48	65·65	65·82	66·17	66·35	66·52	66·70	66·88
67	66·12	66·30	66·47	66·64	66·82	67·18	67·35	67·53	67·71	67·89
68	67·10	67·29	67·46	67·64	67·82	68·18	68·36	68·54	68·72	68·90
69	68·09	68·28	68·45	68·63	68·82	69·18	69·36	69·54	69·73	69·91
70	69·08	69·26	69·44	69·63	69·82	70·18	70·37	70·55	70·74	70·92
71	70·07	70·25	70·43	70·62	70·81	71·19	71·37	71·56	71·75	71·94
72	71·05	71·24	71·43	71·62	71·81	72·19	72·38	72·57	72·76	72·95
73	72·04	72·23	72·42	72·61	72·81	73·19	73·38	73·57	73·77	73·97
74	73·03	73·22	73·41	73·61	73·80	74·19	74·39	74·58	74·78	74·98
75	74·01	74·21	74·40	74·60	74·80	75·20	75·39	75·59	75·79	75·99
76	75·00	75·20	75·40	75·60	75·80	76·20	76·40	76·60	76·80	77·01
77	75·99	76·19	76·39	76·59	76·79	77·20	77·40	77·60	77·81	78·02
78	76·97	77·18	77·38	77·58	77·79	78·20	78·41	78·61	78·82	79·03
79	77·96	78·17	78·37	78·58	78·79	79·21	79·41	79·62	79·83	80·04
80	78·94	79·16	79·36	79·58	79·79	80·21	80·42	80·63	80·84	81·06
81	79·93	80·15	80·35	80·57	80·79	81·21	81·42	81·64	81·85	82·07
82	80·92	81·14	81·35	81·56	81·78	82·21	82·43	82·65	82·87	83·09
83	81·91	82·13	82·34	82·56	82·78	83·22	83·44	83·66	83·88	84·10
84	82·90	83·12	83·34	83·56	83·78	84·22	84·44	84·66	84·89	85·11
85	83·88	84·11	84·33	84·55	84·78	85·22	85·45	85·67	85·90	86·13
86	84·87	85·10	85·32	85·55	85·78	86·22	86·46	86·67	86·91	87·14
87	85·85	86·08	86·31	86·54	86·77	87·23	87·46	87·68	87·92	88·15
88	86·84	87·07	87·30	87·54	87·77	88·23	88·47	88·69	88·93	89·17
89	87·82	88·06	88·29	88·53	88·77	89·23	89·47	89·70	89·94	90·18
90	88·81	89·05	89·29	89·52	89·77	90·23	90·48	90·71	90·95	91·19
91	89·90	90·04	90·28	90·52	90·76	91·24	91·48	91·72	91·96	92·21
92	90·79	91·03	91·27	91·51	91·76	92·24	92·49	92·73	92·97	93·22
93	91·77	92·02	92·26	92·51	92·76	93·24	93·49	93·74	93·98	94·23
94	92·76	93·01	93·26	93·50	93·75	94·24	94·49	94·74	94·99	95·24
95	93·74	94·00	94·25	94·50	94·75	95·25	95·50	95·75	96·00	96·26
96	94·73	94·98	95·24	95·49	95·75	96·25	96·51	96·76	97·01	97·27
97	95·72	95·97	96·23	96·49	96·75	97·25	97·51	97·77	98·02	98·29
98	96·70	96·96	97·22	97·48	97·74	98·25	98·52	98·77	99·03	99·30
99	97·69	97·95	98·21	98·48	98·74	99·26	99·52	99·78	100·04	100·31
100	98·68	98·95	99·21	99·47	99·74	100·26	100·53	100·79	101·05	101·32

TABLE IV.

Table of the Pressure of (Saturated) Water Vapour in mm. of Mercury.

°C.	mm.	°C.	mm.	°C.	mm.
− 20	0·96	24	22·3	66	195·9
− 10	2·16	25	23·7	68	214·0
− 5	3·17	26	25·1	70	233·5
− 2	3·96	27	26·7	72	254·5
− 1	4·26	28	28·3	74	277·1
0	4·58	29	29·9	76	301·3
+ 1	4·92	30	31·7	78	327·2
2	5·29	31	33·6	80	355·1
3	5·68	32	35·5	82	384·9
4	6·09	33	37·6	84	416·7
5	6·54	34	39·8	86	450·8
6	7·01	35	42·0	88	487·1
7	7·51	36	44·4	90	525·8
8	8·04	37	46·9	92	567·1
9	8·60	38	49·5	94	611·0
10	9·21	39	52·3	96	657·7
11	9·84	40	55·1	98	707·3
12	10·51	42	61·3	100	760·0
13	11·23	44	68·0	102	815·9
14	11·98	46	75·4	104	875·1
15	12·78	48	83·5	106	937·9
16	13·63	50	92·3	108	1004·0
17	14·52	52	101·9	110	1075·0
18	15·46	54	112·3	112	1149·0
19	16·46	56	123·6	114	1227·0
20	17·5	58	135·9	116	1310·0
21	18·6	60	149·2	118	1397·0
22	19·8	62	163·6	120	1489·0
23	21·0	64	179·1		

TABLE V.

International Atomic Weights (1921).

	weight.	Atomic Symbol.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	70·1
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6

	weight.	Atomic Symbol.
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·008
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	45·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·15
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89·33
Zinc	Zn	65·37
Zirconium	Zr	90·6

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